

THE PROCEEDINGS OF THE PHYSICAL SOCIETY

Section A

VOL. 64, PART 10

1 October 1951

No. 382 A

Experiments on the Production of Very Low Temperatures by Two-Stage Demagnetization

BY J. DARBY, J. HATTON, B. V. ROLLIN, E. F. W. SEYMOUR
AND H. B. SILSBEE
Clarendon Laboratory, Oxford

MS. received 5th June 1951

ABSTRACT. A two-stage demagnetization apparatus employing a superconducting wire as the thermal switch between the stages is described. Temperatures in the region of 0.003°K. have been obtained using a magnetic field of only 4,200 gauss. The problem of thermal insulation was investigated and the residual heat inflow after demagnetization was reduced to one erg/min. The possibility of employing a superconducting switch in cyclical magnetic cooling systems and in nuclear demagnetization is discussed.

§1. INTRODUCTION

THE success of the method of cooling by adiabatic demagnetization depends to a large extent on the amount of entropy which is removed in the initial isothermal magnetization. In order to remove an appreciable fraction of the electron spin entropy in a magnetic field H at temperature T we require a value of H/T greater than about 15 kilogauss per degree. The magnetization is normally carried out at about 1°K. , which is the lowest temperature obtainable by pumping liquid helium, and large water-cooled magnets are necessary to produce the required field. The use of such large magnetic fields could be avoided by employing a two-stage process in which the magnetization of the second stage is carried out at a temperature lower than 1°K. obtained by demagnetization of the first stage.

The practical realization of a two-stage process has been impeded by the technical difficulty of obtaining a satisfactory way of making and breaking thermal contact between the stages. In experiments by Mendoza (1948) contact between two magnetic stages was made by copper foil which was mechanically broken after magnetization of the second stage. These experiments demonstrated the possibility of the method, but the subsequent heating of the second stage was exceptionally rapid.

Experiments on the thermal conductivity of superconductors at low temperatures (de Haas and Rademakers 1940, Rademakers 1949, Hulm 1949, Heer and Daunt 1949, Mendelssohn and Olsen 1950) have led to the development of an alternative method for obtaining a satisfactory thermal switch. This depends on the fact that for some pure superconductors there is a considerable

difference between the thermal conductivity in the superconducting and non-superconducting states.

We have made a number of experiments with a two-stage apparatus, based on the application of this property. The apparatus was designed to enable temperatures below a hundredth of a degree to be obtained, using a low-power magnet giving a field of only about four kilogauss.

§2. THE THERMAL SWITCH

In a normal metal, at temperatures sufficiently low for the mean free path of the conduction electrons to be independent of temperature, one would expect the thermal conductivity to be proportional to the temperature. For a superconducting metal the electrons in the superconducting state make no contribution to the thermal conductivity, so that at temperatures appreciably below the transition temperature the conductivity should be of the same order as that of a non-metal and should vary as the cube of the temperature. According to Heisenberg's theory of superconductivity (Heisenberg 1949), the ratio of the conductivities in the superconducting and normal states is given approximately by $K_s/K_n = 2(T/T_c)^3/[1 + (T/T_c)^4]$, where T_c is the superconducting transition temperature.

In experiments by de Haas and Rademakers (1940) it was shown that the thermal conductivity of lead was much less when in the superconducting state than when the superconductivity was destroyed by application of a magnetic field in excess of the threshold value. At temperatures below 4°K. the conductivity in zero field was very small and, as the temperature was lowered, decreased approximately as T^3 . Measurements by Heer and Daunt (1949) on tin and tantalum have confirmed that the ratio of the conductivities in the superconducting and normal states is approximately proportional to $(T/T_c)^2$ for $T \ll T_c$. It has, however, been found by Mendelssohn and Olsen (1950) that quite different results are obtained for columbium and also for superconducting alloys, so that it appears that the relation is valid only for certain pure superconductors.

The application of a magnetic field to a superconducting wire as a method for varying the thermal contact between specimens in demagnetization experiments was suggested by Gorter (1948), and experiments demonstrating the use in a single stage apparatus have been made by Heer and Daunt (1949). In the experiments of Heer and Daunt a paramagnetic salt was connected to a helium cryostat at 1.1°K. by a tantalum wire. When the salt was at a temperature in the region of 0.6°K., the rate of heat inflow when the wire was superconducting was about twenty times smaller than when the superconductivity was destroyed by a magnetic field.

For a satisfactory thermal switch it is clearly desirable to have the highest possible ratio between the normal and superconducting thermal conductivities. If T_1 and T_2 are the temperatures of the ends of the wire, and if the conductivities K_s and K_n in the two states vary as T^3 and T respectively, then if $T_1 \gg T_2$ the rate of heat flow in the two cases is approximately proportional to T_1^4 and T_1^2 , so that the ratio varies as T_1^2 . As a rough approximation this ratio can be equated to $(T_1/T_c)^2$, so that in order to obtain a ratio of 1:1,000 the temperature of the warmer end of the wire should not exceed about one-thirtieth of the transition temperature.

§3. CHOICE OF PARAMAGNETIC SALTS

The considerations affecting the choice of the paramagnetic salts for a two-stage apparatus are rather different for the two stages. For the first stage we require: (i) the entropy removed on magnetization to be large and, in any case, to be considerably greater than the entropy of magnetization of the second stage; (ii) the temperature after demagnetization to be low enough to enable an appreciable degree of magnetic saturation of the second stage to be obtained with the available field. For our purpose it appeared that the most suitable substance to use was iron ammonium alum.

For the second stage we require a salt which will attain a very low temperature when demagnetized from conditions approaching magnetic saturation. In the ideal case, the temperature should be determined only by the magnetic interaction of the ions, which could, if necessary, be reduced by dilution. In practice, other effects, such as exchange interaction, Stark effect and interactions between electrons and nuclei are often the limiting factors. In the preliminary experiments (Darby, Hatton and Rollin 1950) we used diluted copper potassium sulphate, but there are considerable nuclear and exchange interactions in this salt (Benzie and Cooke 1949), and in subsequent experiments we decided it would be better to use dilute mixed crystals of potassium aluminium alum and potassium chrome alum, containing 5% of potassium chrome alum. Although this substance is not free from all defects it is reasonably satisfactory and, furthermore, its thermal and magnetic properties at very low temperatures have already been investigated (de Klerk, Steenland and Gorter 1950).

§4. DESCRIPTION OF THE APPARATUS

The two stages were cylinders of compressed salt, the first stage of diameter 16 mm. and length 5.7 cm., and the second stage of diameter 9 mm. and length 2.3 cm. The cylinders were suspended in a framework by an axial cotton thread

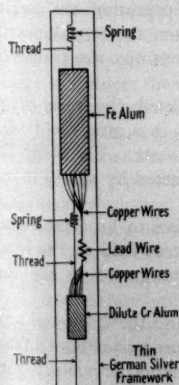


Figure 1.

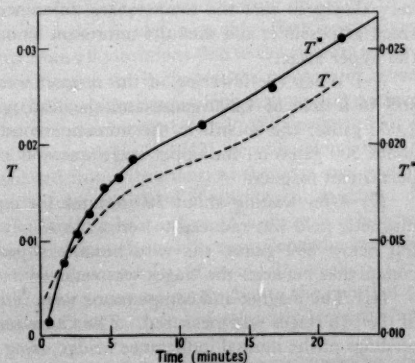


Figure 2.

which was maintained in tension by springs (Figure 1). Each cylinder was provided with six copper wires of diameter 0.2 mm. around which the salt was tightly compressed. These wires enabled thermal contact to be made between

the salt and the lead wire which served as the thermal switch. The lead wire was made from lead of the highest purity obtainable and was of length about 3 cm. and diameter 0.3 mm.; it was situated midway between the cylinders.

The framework containing the two stages was inserted into the helium cryostat through a ground joint at the lower end which was sealed with glycerine.

The magnetic susceptibility, and hence the Curie temperature, of each stage was obtained by measuring the mutual inductance between coils mounted outside the cryostat. The separation between the stages was such that the upper salt had no disturbing influence on the measurement of the susceptibility of the lower salt. The magnetic dilution of the second stage was great enough to make correction of the T^* values, due to the non-spherical shape of the specimen, negligible. The measurement of mutual inductance was made by means of an audio-frequency bridge of the Hartshorn type operated at a frequency of 25 c/s.

The magnet used had pole faces 6 in. high and 4 in. wide with a pole gap of 2 in., and gave a field of 4,200 gauss with a power consumption of 600 watts. The height of the pole faces was sufficient to enable both stages to be magnetized simultaneously, which is a desirable, though not essential, feature.

§ 5. EXPERIMENTAL PROCEDURE

(i) The temperature of the cryostat was reduced to about 1°K . and both stages were magnetized in a field of 4,200 gauss, the heat of magnetization being removed by helium exchange gas at a pressure of about 5×10^{-4} mm. Hg.

(ii) After about 10 minutes the exchange gas was pumped away and the pumping continued for a further 30 minutes in order to remove as much as possible of the gas adsorbed on the surface of the cryostat.

(iii) The magnet was slowly lowered so that the upper stage was demagnetized while the lower stage remained in the field. During this time the lead wire was in a field greater than the threshold value and, as the cooling proceeded, heat was transferred from the lower stage to the upper. This operation was carried out very slowly so that the temperature difference between the two stages was as small as possible, and thus the minimum amount of entropy was transferred to the upper stage.

(iv) When the lowering of the magnet was completed, the lower stage was still in a field of 4,200 gauss and the lead wire was in a stray field of about 1,000 gauss, and so still in the non-superconducting state. The stray field of about 500 gauss on the upper stage was now compensated by means of a small permanent magnet.

(v) After waiting about 30 minutes for equilibrium to be established, the magnetic field was reduced to zero. As soon as the stray field on the lead wire fell below 800 gauss, the wire became superconducting and so the thermal conduction between the stages was reduced.

(vi) The magnet and compensator were removed and the Curie temperature of the two stages was measured. The Curie temperature was obtained from the readings of the mutual inductance bridge using a calibration previously obtained in the temperature region between 4.2°K . and 1.5°K .

§ 6. RESULTS

The lowest Curie temperature reached after demagnetization was about 0.009° . From the measurements of de Klerk, Steenland and Gorter (1950) this corresponds to an absolute temperature of about 0.003°K . In order to

obtain this temperature in a single stage demagnetization from 1.05°K . a magnetic field of 15,200 gauss would be required. The temperature of the upper stage was about 0.25°K .

In the initial experiments the heating rate of the second stage after demagnetization was rather rapid, being sometimes as high as 50 erg/min. However, after a number of modifications had been made to the apparatus, a heating rate of only about 1 erg/min. was obtained. In Figure 2 is shown a typical heating curve for the second stage. The temperature remained below a hundredth of a degree for about 3 minutes. The heating rate of the first stage was negligible, being only of the order of 1.5×10^{-4} degree per minute, corresponding to a heat inflow of 50 erg/min.

§ 7. EXPERIMENTS ON HEAT INFLOW

In experiments at very low temperatures one of the most important considerations is the rate of heat inflow to the specimen. In previous experiments by Cooke and Hull (1942) it has been shown that with suitable experimental arrangements the heat inflow can be reduced to the order of one erg per minute, though other workers, in this and other laboratories, have usually observed much larger heat inflows.

The high heat inflow which was observed in our initial experiments was first attributed to conduction along the superconducting wire. Experiments with different lengths of wire, however, disproved this hypothesis. In order to find whether the heat inflow was due to the presence of residual gas in the cryostat and to conduction along the supporting threads, the apparatus was modified so that the lower stage was surrounded by a copper cylinder which was soldered to wires embedded in the upper stage. In this arrangement the lower stage was completely shielded from any heat inflow from the cryostat. Although this arrangement made some improvement, the heat inflow was still large. After a number of further experiments, the origin of the anomalous heating was finally traced to the effects of small vibrations which produced heating due to frictional losses in the suspended system. In order to eliminate this effect it was found necessary to insulate the apparatus from all vibrations due to the vacuum pumps. It was found that even the vibration due to the boiling of the mercury of a small diffusion pump caused a heating of the upper stage of more than 300 erg/min. A similar effect has been observed in experiments by Hull, Wilkinson and Wilks (1951). In the experiments of Cooke and Hull (1942) we understand that the cryostat was, by chance, well insulated from vibrations, so that this may account for the discrepancy between their results and those of subsequent workers.

It is of interest to note that the limiting heat inflow of 1 erg/min. which was finally obtained is about 60 times less than the conduction along the lead wire calculated by extrapolation of the measurements of de Haas and Rademakers (1940) according to a T^3 law. This discrepancy may be partly due to the fact that the specimen used by these authors was a single crystal of relatively large diameter (2.5 mm.).

Some rough measurements were made of the heat inflow to the lower stage when a field greater than the threshold value was applied to the lead wire by means of a small permanent magnet. With the upper stage at 0.3°K . and the lower stage between 0.01° and 0.1° heating rates of the lower stage of more than a hundred ergs per minute were observed. This is consistent with the expectation that the heat flow should be increased approximately as $(T_0/T_1)^2$.

§8. POSSIBILITY OF CYCLICAL PROCESSES

The use of superconducting wires for heat transfer in a cyclical magnetic cooling process has been proposed by Daunt and Heer (1949). It appears to us that some difficulty would be experienced in attempting to operate such a process with a starting temperature as high as 1°K. because the superconductor is not a very efficient thermal switch at this temperature. The main difficulty is that during the period of magnetization, when the salt is at a temperature above 1°K. , a considerable amount of heat is transmitted along the second wire even though it is in the superconducting state.

It would, however, seem practicable to operate a cyclical process starting from a lower temperature, say in the region of 0.2°K. , using as a heat reservoir a large quantity of a suitable paramagnetic salt such as iron alum. In this way it should be possible, with a single stage cyclical process, to maintain a temperature of about a hundredth of a degree for several hours provided the heat influx from external sources were not more than a few ergs per minute.

Although our apparatus was not designed for cyclical operation, we have found it possible to carry out several successive demagnetizations of the second stage without remagnetizing the first stage. It seems that an apparatus of the kind we have described could, with minor modifications, be adapted for operation as a cyclical system.

§9. APPLICATION TO NUCLEAR DEMAGNETIZATION

It has been suggested (Gorter 1934, Kurti and Simon 1935, Simon 1939) that it should be possible to extend the lower limit of temperature attainable by the use of nuclear paramagnetism instead of electron paramagnetism. Since nuclear magnetic moments are of the order of one thousandth of the electron moment, it is impossible to remove an appreciable amount of nuclear spin entropy at 1°K. by the application of any practically realizable magnetic field. The magnetization must be carried out at a temperature lower than 0.01°K. , so that the use of an initial stage of electronic demagnetization is essential.

It seems that the superconducting switch would be well adapted for controlling the flow of heat between the nuclear stage and the electronic stage. At such low temperatures an extremely high on-off ratio for the superconducting switch should be obtainable. One practical difficulty is that, in order to remove the heat of nuclear magnetization in a reasonable time, a large cross section of metal, of the order of 1cm^2 , would be required. Some difficulty might also be experienced in establishing adequate thermal contact between the metal of the switch and the paramagnetic salt of the first stage.

Even at a temperature of 0.01°K. a magnetic field of the order of 50 kilogauss would be necessary to remove an appreciable fraction of the nuclear spin entropy. It does not seem practicable to perform a satisfactory nuclear demagnetization by using smaller magnetic fields and more stages of electronic demagnetization to obtain a lower temperature for the nuclear magnetization process. Owing to unavoidable heat inflows, the nuclear stage would need to be an appreciable fraction of a mole in order to remain at the low temperature long enough to enable observations to be made. The requirement that each stage must contain a greater molar fraction than the subsequent one in order to take up the necessary entropy without appreciable rise of temperature means that the first stage would have to be of impracticably large dimensions.

Note added in proof. In more recent experiments with an apparatus similar to that described above, we have used a water-cooled electromagnet giving a field of about 9,000 gauss. The Curie temperature reached by the second stage, which contained 8.4×10^{-4} mole of Cr ions, was 0.0045° . By extrapolation of the results of de Klerk, Steenland and Gorter (1950), this corresponds to an absolute temperature of approximately 10^{-3}°K .

The temperature remained below 0.01°K . for 40 minutes.

ACKNOWLEDGMENTS

Our thanks are due to Professor F. Simon for his interest in this work. One of us (J.H.) wishes to make grateful acknowledgment to the Pressed Steel Company Ltd., Cowley, for a Research Fellowship, E.F.W.S. is grateful to the Department of Scientific and Industrial Research for a research grant, and H.B.S. would like to record his thanks to Harvard University for a Sheldon Travelling Fellowship.

REFERENCES

- BENZIE, R. J., and COOKE, A. H., 1949, *Nature, Lond.*, **164**, 837.
 COOKE, A. H., and HULL, R. A., 1942, *Proc. Roy. Soc. A*, **181**, 83.
 DARBY, J., HATTON, J., and ROLLIN, B. V., 1950, *Proc. Phys. Soc. A*, **63**, 1179.
 DAUNT, J. G., and HEER, C. V., 1949, *Phys. Rev.*, **76**, 985.
 GORTER, C. J., 1934, see DEBYE, P., 1934, *Phys. Z.*, **35**, 923.
 GORTER, C. J., 1948, *Les phénomènes cryomagnétiques* (Paris : Cérémonies Langevin-Perrin), p. 76.
 DE HAAS, W. J., and RADEMAKERS, A., 1940, *Physica*, **7**, 992.
 HEER, C. V., and DAUNT, J. G., 1949, *Phys. Rev.*, **76**, 854.
 HEISENBERG, W., 1949, *Electron Theory of Superconductivity* (Cambridge : University Press).
 HULL, R. A., WILKINSON, K. R., and WILKS, J., 1951, *Proc. Phys. Soc. A*, **64**, 379.
 HULM, J. K., 1949, *Nature, Lond.*, **163**, 368.
 DE KLERK, D., STEENLAND, M. J., and GORTER, C. J., 1950, *Physica*, **16**, 571.
 KURTI, N., and SIMON, F., 1935, *Proc. Roy. Soc. A*, **149**, 152.
 MENDELSSOHN, K., and OLSEN, J. L., 1950, *Proc. Phys. Soc. A*, **63**, 2.
 MENDOZA, E., 1948, *Les phénomènes cryomagnétiques* (Paris : Cérémonies Langevin-Perrin), p. 53.
 RADEMAKERS, A., 1949, *Physica*, **15**, 849.
 SIMON, F., 1939, *Le Magnétisme*, **3**, 1 (Paris : Institut International de Coopération Intellectuelle).

A Note on Fröhlich's Theory of Superconductivity

By KUN HUANG

Department of Theoretical Physics, University of Liverpool

Communicated by H. Fröhlich; MS. received 21st February 1951

ABSTRACT. It is shown that the physical mechanisms underlying the two energy terms E_1 and E_2 in Fröhlich's theory are very different: E_1 is largely the energy change due to a modification of the lattice vibration frequencies caused by the adiabatic deformation of the electrons; E_2 is on the other hand a dynamical term, representing the energy change due to virtual collisions between lattice oscillations and electrons. A proof is given that certain inadmissible consequences of the theory, pointed out recently by Wentzel, derive from the energy term E_1 ; the superconductive behaviour discussed by Fröhlich arises however entirely from the term E_2 . Although both terms follow from the same perturbation treatment, the analysis given makes it seem not unlikely that whatever mechanism actually inhibits E_1 will leave the superconductive behaviour deduced from E_2 not substantially affected.

It is the purpose of the present note to describe certain conclusions as regards Fröhlich's theory (Fröhlich 1950) which have been obtained in the course of the investigations undertaken by the author in active collaboration with Mr. M. J. Buckingham and Mr. B. V. Paranjape of this department; they are such as to give a better understanding of the physical mechanisms underlying the different energy terms in Fröhlich's theory. A clarification of such issues is deemed particularly desirable, for they are closely related to certain points raised recently by Wentzel (1951)*. Wentzel's conclusions can be summarized as follows: (a) the interaction term between the lattice and electrons required for superconductivity is so strong that the convergence of the perturbation method used in Fröhlich's theory is bad; (b) the interaction is of such a magnitude as to cause in some cases an apparent instability in the lattice, which must in practice be prevented by other stabilizing influences such as the Coulomb interactions; these influences should be taken into account in a realistic treatment.

To save space we shall use the original notation in Fröhlich's paper (Fröhlich 1950) without further explanation; hereafter his paper will be referred to as (F).

Fröhlich's treatment refers throughout to the case that none of the lattice vibrations are excited. A significant difference between the energy terms denoted by Fröhlich as E_1 and E_2 emerges, however, when one considers an arbitrary excited state of the lattice. Let us consider the part of these energies contributed by a particular mode $\mathbf{w}$, which is in the quantum state v . We have now to consider the energy terms due to the virtual absorption as well as emission of a phonon. Consider first the terms corresponding to E_2 . The emission terms can be taken directly from (2.14) of (F) by omitting the summation over $\mathbf{w}$ and multiplying by $(v+1)$:

$$\frac{16F\zeta\sigma_0(v+1)}{3n(2\pi)^3} \int \frac{f_{\mathbf{k}}f_{\mathbf{k}-\mathbf{w}}w}{|\mathbf{k}-\mathbf{w}|^2 - k^2 + \sigma_0 w} d\mathbf{k} \quad (\text{emission terms}) \quad \dots\dots(1)$$

where we have expressed $\mathbf{q}$ in (F) explicitly as $\mathbf{k}-\mathbf{w}$. The absorption terms can be obtained from (1) by replacing $(v+1)$ by v , $\mathbf{k}-\mathbf{w}$ by $\mathbf{k}+\mathbf{w}$ and $\sigma_0 w$ in the denominator by $-\sigma_0 w$:

$$\frac{16F\zeta\sigma_0 v}{3n(2\pi)^3} \int \frac{f_{\mathbf{k}}f_{\mathbf{k}+\mathbf{w}}w}{|\mathbf{k}+\mathbf{w}|^2 - k^2 - \sigma_0 w} d\mathbf{k} \quad (\text{absorption terms}). \quad \dots\dots(2)$$

Let us consider the integral in (2). If we express $\mathbf{k}$ in terms of $\mathbf{q}=\mathbf{k}+\mathbf{w}$, the integral becomes

$$\int \frac{wf_{\mathbf{q}-\mathbf{w}}f_{\mathbf{q}}}{q^2 - |\mathbf{q}-\mathbf{w}|^2 - \sigma_0 w} d\mathbf{q},$$

which is clearly the negative of the integral in (1). Thus, adding (1) and (2), we obtain the total contribution to E_2 due to both virtual absorptions and emissions as

$$\frac{16F\zeta\sigma_0}{3n(2\pi)^3} \int \frac{wf_{\mathbf{k}}f_{\mathbf{k}-\mathbf{w}}}{|\mathbf{k}-\mathbf{w}|^2 - k^2 + \sigma_0 w} d\mathbf{k} \quad \dots\dots(3)$$

The point to note is that the expression is independent of the lattice quantum number v .

E_1 , on the other hand, is not independent of the lattice quantum number. The lattice instability as discussed by Wentzel means simply that the energy of the system can be lowered indefinitely by increasing indefinitely the lattice quantum number. This situation can only be caused by terms dependent on the lattice quantum number; Wentzel's considerations thus concern only the E_1 term.

* I am grateful to Professor Fröhlich for access to Professor Wentzel's work before its publication.

The contribution to E_1 due to a particular mode w in state v , when worked out explicitly, is given by

$$\left. \begin{aligned} & -\frac{F\zeta\sigma_0}{3n(2\pi)^2}(v+1)\left\{[4k_0^2-(w+\sigma_0)^2]\ln\left|\frac{2k_0+\sigma_0+w}{2k_0-\sigma_0-w}\right|+4k_0(w+\sigma_0)\right\} \\ & -\frac{F\zeta\sigma_0v}{3n(2\pi)^2}\left\{[4k_0^2-(w-\sigma_0)^2]\ln\left|\frac{2k_0-\sigma_0+w}{2k_0+\sigma_0-w}\right|+4k_0(w-\sigma_0)\right\}, \end{aligned} \right\} \dots\dots(4)$$

where the two lines correspond respectively to the emission and the absorption terms.

For lattice waves long compared with the lattice constant, we expand (4) with respect to w and ignore second and higher order terms:

$$-\frac{4F\zeta k_0\sigma_0^2}{3n(2\pi)^2}-\frac{8F\zeta k_0\sigma_0}{3n(2\pi)^2}(2v+1)w. \dots\dots(5)$$

The excitation energy of the lattice vibration in state v is given on the other hand by

$$(v+\frac{1}{2})\hbar\omega_s. \dots\dots(6)$$

On combining (5) and (6), we find

$$-\frac{4F\zeta k_0\sigma_0^2}{3n(2\pi)^2}+(v+\frac{1}{2})\hbar\omega\left\{s-\frac{16F\zeta k_0\sigma_0}{3n(2\pi)^2\hbar}\right\} \dots\dots(7)$$

which, we note, includes all terms dependent on v . When the coefficient of the second term is positive, the term is equivalent to a reduction of the sound velocity from the value s to the value

$$s-\frac{16F\zeta k_0\sigma_0}{3n(2\pi)^2\hbar}=s(1-2vF). \dots\dots(8)$$

If however (8) is negative, the energy of the system can be indefinitely reduced by increasing v . This is the instability discussed by Wentzel.

To obtain a better understanding of this change of sound velocity let us suppose as a pure hypothesis that during a lattice vibration the electrons are merely deformed adiabatically. At every instant, we would thus imagine the electrons as being subject to a *static* perturbation corresponding to the instantaneous configuration of the lattice. According to the adiabatic approximation, the corresponding electronic energy operates as an additional potential function for the lattice motion. We wish to determine this potential function and find out how it modifies the lattice motion.

As in (F), we have so far been using the normal coordinates introduced originally by Peierls. In Peierls' scheme (cf. Sommerfeld and Bethe 1933), the lattice displacement is given by

$$\mathbf{u}(\mathbf{x})=\frac{1}{\sqrt{N}}\sum_{\mathbf{w}}\mathbf{e}_{\mathbf{w}}\{a_{\mathbf{w}}\exp(i\mathbf{w}\cdot\mathbf{x})+a_{\mathbf{w}}^*\exp(-i\mathbf{w}\cdot\mathbf{x})\} \quad (\mathbf{e}_{\mathbf{w}}=\mathbf{e}_{-\mathbf{w}})$$

where $\mathbf{e}_{\mathbf{w}}$ is the polarization vector and $a_{\mathbf{w}}, a_{\mathbf{w}}^*$ are respectively the annihilation and creation operators for the normal mode $\mathbf{w}$. These operators depend on the momenta as well as the normal coordinates. The lattice-electron interaction, being constructed from $\mathbf{u}(\mathbf{x})$, depends thus also on the momenta. This fact makes it inconvenient to use Peierls' coordinates to consider the adiabatic modification of lattice motion. Thus instead we shall make use of the more usual normal coordinates $q_{\mathbf{w}}$, which are related to the normalized Fourier coefficients $Q_{\mathbf{w}}$ of $\mathbf{u}(\mathbf{x})$:

$$\mathbf{u}(\mathbf{x})=\frac{1}{\sqrt{N}}\sum_{\mathbf{w}}\mathbf{e}_{\mathbf{w}}Q_{\mathbf{w}}\exp(i\mathbf{w}\cdot\mathbf{x})$$

by $Q_w = Q_w^* = (q_w + iq_{-w})/\sqrt{2}$, w in this relation being restricted to one side of a plane through $w=0$.

Consider now a static deformation due to q_w alone; the corresponding lattice displacement is given by

$$u(\mathbf{x}) = \frac{1}{\sqrt{N}} \mathbf{e}_w q_w \frac{1}{\sqrt{2}} \{ \exp(i\mathbf{w} \cdot \mathbf{x}) + \exp(-i\mathbf{w} \cdot \mathbf{x}) \}. \quad \dots\dots(9)$$

Let us contrast it with the expression in Peierl's scheme:

$$u(\mathbf{x}) = \frac{1}{\sqrt{N}} \mathbf{e}_w \{ a_w \exp(i\mathbf{w} \cdot \mathbf{x}) + a_w^* \exp(-i\mathbf{w} \cdot \mathbf{x}) \} \quad \dots\dots(10)$$

which underlies our earlier considerations of the contributions to E_1 and E_2 due to a single Peierls mode w . We note that (10) would reduce to (9) if we replace both a_w and a_w^* by $q_w/\sqrt{2}$. This fact makes it possible to obtain the electronic energy (in the approximation of a second order perturbation calculation) due to the static deformation (9), from the expressions for E_1 and E_2 by suitable replacements. The second order terms due to the static perturbation have a strict correspondence with the terms in $E_1 + E_2$. Now as the normal coordinate q_w is to be considered as a parameter and we are only concerned with virtual electronic transitions, we have to delete the $\sigma_0 w$ term in the denominators of (2.13), (2.14) in (F). Moreover, in the absorption and emission terms of E_1 and E_2 we have incorporated the squared transition matrix elements of a_w and a_w^* :

$$\left(\frac{\hbar}{2wsM} \right) \begin{Bmatrix} v \\ v+1 \end{Bmatrix} \quad \dots\dots(11)$$

In view of (9) and (10), for the static perturbation, both of these squared matrix elements should be replaced by

$$(q_w/\sqrt{2})^2. \quad \dots\dots(12)$$

Consider first the static perturbation terms analogous to E_1 . Putting $\sigma_0 = 0$ in the denominator of (2.13) of (F) is equivalent to putting $\sigma_0 = 0$ in the brackets in (4); and the replacement of (11) by (12) is equivalent to replacing both $(v+1)$ and v in (4) by $Mswq_w^2/\hbar$. Thus we obtain from (4) the corresponding expression for the static perturbation as

$$-\frac{2MF\zeta\sigma_0sw}{3n(2\pi)^2\hbar} q_w^2 \left\{ (4k_0^2 - w^2) \ln \left| \frac{2k_0 + w}{2k_0 - w} \right| + 4k_0w \right\}.$$

Expanding for long waves, we find

$$-\frac{16F\zeta k_0\sigma_0}{3n(2\pi)^2\hbar} Msw^2q_w^2 = -2\nu FMs^2w^2q_w^2.$$

If we add this additional potential function due to the adiabatic deformation of the electronic state to the potential function of the mode q_w , viz. $\frac{1}{2}M(ws)^2q_w^2$, we obtain the modified harmonic potential:

$$\frac{1}{2}M \{ w^2s^2(1 - 2\nu F^2) \} q_w^2, \quad \dots\dots(13)$$

where we have completed the square by adding a term in F^2 , which is formally permissible in view of the perturbation procedure we have used. The adiabatic consideration leads thus to exactly the same change in the sound velocity as (8).

This shows that at least for the longer waves E_1 describes merely an adiabatic deformation of the electrons by the lattice vibrations.

We have not yet considered the static perturbation terms analogous to E_2 . Such terms however vanish identically. For we have to replace $v+1$ and v both by the same factor $(M\omega/\hbar)q_\omega^{-2}$ in (1) and (2) and add the two expressions. The sum vanishes, as we have shown that the two integrals are equal and opposite in sign. The E_2 term is thus not involved in the adiabatic deformation of the electronic state.

The difference between the underlying physical mechanisms of the E_1 and E_2 terms in Fröhlich's theory is now clear: E_1 is mainly the energy change due to the modifications in the lattice frequencies, caused by the adiabatic deformation of the electrons. E_2 is on the other hand a purely dynamical effect, representing the energy change of the electrons due to virtual collisions with the lattice vibrations.

From a purely practical viewpoint, while the large lattice frequency changes following from E_1 are almost certain to be inhibited by some mechanism, E_2 is not to be similarly suppressed. For the latter is clearly related closely to the electron scattering responsible for electrical resistivity. In view of the essential difference between the mechanisms responsible for the two energy terms as well as the fact that E_1 depends on the lattice vibration quantum number, whereas E_2 does not, one is thus inclined to the belief that whatever mechanism ultimately inhibits E_1 will not seriously affect E_2 . In this connection, one may note the heuristic advantage of the use of the experimental resistivity values in the numerical estimates given in Fröhlich's paper.

A discussion of the effect of the Coulomb interaction between the electrons is given at the end of the Appendix. Effects due to the correlation between electrons are still being investigated.

It need hardly be emphasized that this note does not provide an unequivocal answer to the points raised by Wentzel. But the analysis given should make us better able to assess the situation and may serve as a pointer for further investigations.

It is a pleasure for me to express my thanks to Professor H. Fröhlich and Mr. M. J. Buckingham for stimulating discussions. My thanks are also due to Mr. B. V. Paranjape who has undertaken some calculations in connection with the investigation.

APPENDIX

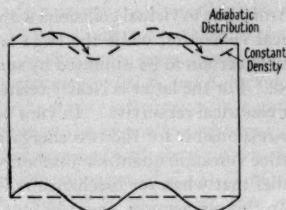
THE ADIABATIC DEFORMATION OF ELECTRONS BY LATTICE VIBRATIONS

For his considerations, Wentzel has employed Tomonaga's boson treatment (Tomonaga 1950) of the electronic motion, which holds for a linear case if the electron density does not vary appreciably within a length of the order of the lattice constant (or average electron distance, to be more precise). We wish to point out briefly the simple underlying physical picture, as it further illuminates the above interpretation of E_1 . However, we shall omit all mathematical details and report only on the results of our investigations.

It is found that Tomonaga's method is completely equivalent to the use of the Thomas-Fermi method in each small neighbourhood. That he can use it for

dynamical problems is the exact parallel of the usual practice in classical continuum physics. If one takes for instance his density waves for free electrons, one finds that the frequencies are exactly reproduced by the pressure waves corresponding to the compressibility of a free Fermi gas (in the completely degenerate state).

When the interaction between the electrons and the lattice is introduced, two types of harmonic vibrations appear in the Tomonaga scheme corresponding to lattice vibrations perturbed by electrons, and to electron pressure waves perturbed by the lattice. When we examine the former type of solutions closely, the following simple picture emerges: When a lattice wave passes, we can think of the bottom of the potential well enclosing the electrons as being warped (solid line along the bottom of Figure). If the electron density is kept constant as before (top of the



distribution indicated by dotted line in Figure), obviously no net energy change results from the interaction, for half of the electrons have their energies raised, and the other half have their energies lowered. The reduction of the lattice frequencies in Tomonaga's method arises from the circumstance that the electrons flow from the energy ridges to the energy troughs, so that the top of the distribution is kept level (solid line in Figure). In the sense of the Thomas-Fermi method, the electrons follow the lattice motions so that at every instant the electrons occupy the lowest states in the instantaneous lattice potential; thus the Tomonaga solution corresponds strictly to an adiabatic treatment of the electrons. As shown by Wentzel, it leads to the possibility of instability; it is clearly equivalent to the E_1 term which we have discussed.

That such considerations should lead to a distinct type of stability condition is only to be expected. For it is associated with the flow of electrons from one volume element to another, a situation not to be realized in a static and homogeneous elastic deformation. Clearly such instability owing to electron flow will in reality be prevented by space-charge effects.

It is a straightforward matter to generalize the stability condition as following from Tomonaga's method to the three-dimensional case. We need only observe that the one-dimensional result can be realized in an extremely simple manner: we consider two equal pieces of metal, one is subject to a uniform dilation, the other to a compression, while free passage of electrons is allowed. Instability occurs in this 'two-piece model' if the lowering of energy due to electron flow exceeds the elastic strain energy in the lattice due to the compression and dilation. We have introduced an explicit lattice-electron interaction by assuming that the change in lattice potential for electrons is at every point proportional to the linear strain. With this explicit interaction, we have verified that the instability condition in the 'two-piece model' is the same as the condition for vanishing lattice frequencies in

the Tomonaga treatment. The three-dimensional analogue follows thus directly by replacing the linear metals in the 'two-piece model' by two boxes.

Using Tomonaga's method, Wentzel has found that if the Coulomb interaction between the electrons is taken into account, the instability due to long waves is prevented. The three-dimensional case is similar: Mr. Paranjape has investigated this case by considering a density wave through the lattice and treating the electrons by the Thomas-Fermi method. He finds that the electron density bears to the ion density the constant ratio $(-C + 4\pi e^2 n_{el}/w^2)/(2\zeta/3 + 4\pi e^2 n_{el}/w^2)$. It is immediately verified that if the wavelength $2\pi/w$ is large compared with the lattice constant, the terms with e^2 predominate and the ratio is practically equal to unity. In other words, in the longer waves the Coulomb interaction prevents the electron flow as envisaged in the Figure and the adiabatic energy change is thus completely suppressed.

Concerning the effect of the Coulomb interaction on the energy E_2 , we may cite the calculation for the resistivity of some metals made a long time ago by Bardeen (1937), who has used the self-consistent field of the electrons as the scattering field. His treatment thus incorporates the effect of the adiabatic deformation of the electrons whereby the Coulomb interaction is taken into account. He found resistivity values smaller, but not drastically so, as compared with results obtained by conventional methods; the latter, we note, are comparable with the method used in deriving E_2 . From this we may infer that the Coulomb interaction, while preventing the instability of the longer waves, will not drastically affect the value of E_2 .

From (4) we readily find that waves with w comparable with k_0 are also subject to instability, for values of F somewhat larger than the critical values for the longer waves. We are investigating whether the exchange effect in a treatment such as that used in Bardeen's resistivity calculation is capable of suppressing the instability of these shorter waves.

REFERENCES

- BARDEEN, J., 1937, *Phys. Rev.*, **52**, 688.
 FRÖHLICH, H., 1950, *Phys. Rev.*, **79**, 845.
 SOMMERFELD, A., and BETHE, H., 1933, *Handb. d. Phys.*, **24**, Part 2, 500.
 TOMONAGA, S., 1950, *Progr. Theor. Phys.*, **5**, 544.
 WENTZEL, G. 1951, *Phys. Rev.*, **83**, 168.

Scintillations from Organic Crystals: Specific Fluorescence and Relative Response to Different Radiations

By J. B. BIRKS

Department of Natural Philosophy, The University, Glasgow*

MS. received 12th April 1951

ABSTRACT. The scintillation response S of organic crystals depends on the nature and energy E of the incident ionizing particle, of residual range r . The specific fluorescence dS/dr is not in general proportional to the specific energy loss dE/dr . By considering the quenching effect of the molecules damaged by the particle on the 'excitons' produced by it, it is shown that $dS/dr = (A dE/dr)/(1 + kB dE/dr)$. A and kB are constants, which have been evaluated for anthracene from observations of S and E , and the range-energy data. Curves are computed for the relative response S of anthracene to electrons, protons, deuterons and α -particles of E up to 15 mev., and these are shown to agree closely with the available experimental results. The method used for evaluating the relative response is applicable to ionizing particles of any nature or energy, and also to the other organic scintillation crystals.

§1. INTRODUCTION

IONIZING radiations impinging on a fluorescent material produce short individual light flashes, or scintillations. These scintillations can be detected with a photo-multiplier tube, and converted into electrical pulses, which can be counted and measured by standard electronic methods. This technique of scintillation counting is being widely applied for the detection and measurement of nuclear radiations. The fluorescent organic crystals are of particular interest for scintillation counting, since they combine a reasonable fluorescent efficiency with a high transparency and a very short luminescent decay time, of the order of 10^{-8} second. These properties make them suitable for the detection of the more penetrating nuclear radiations, and for studies of fast nuclear and meson decay processes, and much of the previous work in this field has been primarily concerned with such applications. The nature of the scintillation process has received rather less attention, and it is, therefore, proposed in this and subsequent papers to consider various fundamental aspects of the fluorescence produced in organic crystals by ionizing radiations.

§2. RESPONSE TO DIFFERENT RADIATIONS

The intensity of the scintillations produced in anthracene and other organic fluorescent crystals depends both on the energy and on the nature of the incident ionizing particle. The amplitude S (volts) of the voltage pulse from a photo-multiplier, operating under constant conditions and observing the crystal, is proportional to the number of fluorescent quanta produced, and hence S may be used as an arbitrary measure of the scintillation intensity. For electrons of energy greater than 125 kev., the scintillation intensity S from an anthracene crystal increases linearly with the energy E (Hopkins 1951), so that the fluorescent efficiency dS/dE (volts/mev.) is constant. For electrons of lower energy, however,

* Now at the Physics Department, Rhodes University, Grahamstown, South Africa.

the efficiency dS/dE is reduced. With heavier particles, which produce more intense ionization, a further reduction in dS/dE occurs, and the scintillation intensity is consequently less than that produced by an electron of the same energy.

It has been noted previously (Birks 1950 a) that the response to different ionizing particles can be readily compared by considering the variation of the specific fluorescence dS/dr (v/cm. air equivalent), which is proportional to the number of fluorescent quanta emitted per unit path length, with the specific energy loss dE/dr (mev/cm. air equivalent), where r (cm. air equivalent) is the residual range of the particle. At low values of dE/dr (electrons of $E > 125$ kev.) the specific fluorescence is proportional to the specific energy loss, corresponding to S increasing linearly with E . At high values of dE/dr (α -particles of $E < 5$ mev.) dS/dr is practically constant and independent of the specific energy loss. The scintillation intensity S is thus proportional to the residual range r of the particle, rather than to its energy E .

§ 3. THEORY

The variation of dS/dr with dE/dr may be readily accounted for on the 'exciton' theory introduced by Bowen *et al.* (1949) to account for the fluorescence of mixed crystals, excited by ultra-violet radiation. On this theory of the energy transfer processes in organic crystals, the electronic energy excited by the incident radiation is transferred from molecule to molecule within the crystal, until it is captured by a single molecule, which then either fluoresces or quenches the 'exciton', depending on the nature of the molecule. This theory has been successfully applied to the energy transfer in mixed crystals of naphthalene and anthracene excited by α -radiation, where both molecular components fluoresce, but the anthracene molecules have the higher 'exciton' capture probability (Birks 1950 b). It has also been used to explain the deterioration of the fluorescent efficiency of anthracene under prolonged α -particle irradiation (Birks and Black 1951). In this case, the molecules damaged by the preceding α -particle irradiation act as quenching agents, having a higher 'exciton' capture probability than the undamaged anthracene molecules.

A similar effect will also occur with individual ionizing particles. The passage of the particle through the crystal produces a local concentration of damaged or ionized molecules along its path. These damaged molecules act as quenching agents for the 'excitons' produced by the ionizing particle. The number of 'excitons' produced per unit path length is proportional to the specific energy loss, say $A dE/dr$. The local concentration of damaged molecules at any point on the particle track is also proportional to the specific energy loss, say $B dE/dr$ molecules per undamaged molecule. Hence, if the 'exciton' capture probability of a damaged molecule, relative to an undamaged molecule, is k , the specific fluorescence

$$\frac{dS}{dr} = \frac{A dE/dr}{1 + kB dE/dr} \quad \dots\dots (1)$$

At low values of dE/dr , (1) becomes $dS/dr = A dE/dr$ and at high values of dE/dr , (1) becomes $dS/dr = A/kB = \text{constant}$, in agreement with the observed behaviour.

The values of A and kB for anthracene have been computed from observations on the relative response to electrons and α -particles reported previously (Birks 1950 a). The residual range r is taken from the range-energy data of Curie (1935) for electrons, and of Livingston and Bethe (1937) and Bethe (1950) for heavier

particles. r is expressed in cm, air equivalent at 15°C. and 760 mm. Hg pressure, but the small correction for the variation of the relative stopping power of anthracene with r has been neglected. This variation is approximately $\pm 1\%$ for $r=0-5$ cm.,

Table 1

Particles	$E(\text{mev.})$	dE/dr	dS/dr
α -particles	2.0	1.8	10.7
Electrons	0.5	0.00215	0.175

and $\pm 2\%$ for $r=5-180$ cm. The specific energy loss dE/dr is expressed in mev/cm. air equivalent. The experimental values used for substitution in (1) are listed in Table 1, giving for anthracene $A=82.5$, $kB=7.15$.

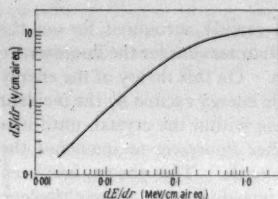


Figure 1. Specific fluorescence dS/dr plotted against specific energy loss dE/dr in anthracene.

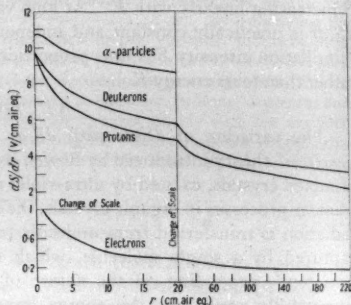


Figure 2. Specific fluorescence dS/dr plotted against residual range r for different particles in anthracene.

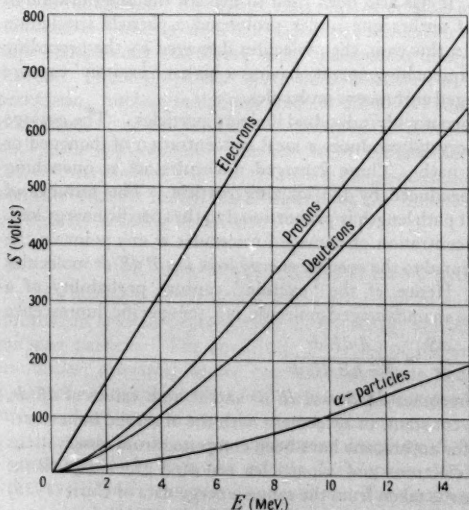


Figure 3. Relative scintillation response S of anthracene to particles of energy E .

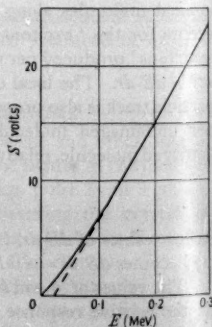


Figure 4. Relative scintillation response S of anthracene to low-energy electrons.

The variation of dS/dr with dE/dr from (1) is plotted in Figure 1. The specific fluorescence dS/dr for different ionizing particles of residual range r has been calculated from (1) and the range-energy data. The results are plotted in Figure 2. The variation of S with r has been obtained by integration of the area below the $(dS/dr, r)$ curves. The scintillation intensity S produced by different ionizing particles of energy E is plotted in Figure 3 and the response to low energy electrons is plotted on an enlarged scale in Figure 4.

§ 4. COMPARISON WITH EXPERIMENTAL DATA

The scintillation response of anthracene to protons of $E \leq 16.4$ mev. has been observed by Franzen *et al.* (1950), to electrons of $E \leq 3.0$ mev. by Hopkins (1951), and to α -particles of $E \leq 5.3$ mev. by Birks (1950 a). In each case the observations agree closely with the predicted responses shown in Figures 3 and 4.

In addition the relative responses of anthracene to different particles have also been reported. A comparison between the experimental response ratios and the predicted values is made in Table 2. The agreement is sufficiently good to establish the general validity of the theory, which may be used to compute the response to any particle.

Table 2

Reference	Particles	Exptl. ratio	Theor. ratio
Harding <i>et al.</i> (1949)	8.78 Mev. α -particles	1.9	1.87
	6.04 Mev. α -particles		
Franzen <i>et al.</i> (1950)	5.3 Mev. α -particles	0.82	0.79
	0.624 Mev. electrons		
	16.4 Mev. protons	16.4	17.5
	0.624 Mev. electrons		
Hofstadter (1950)	5 Mev. protons	~ 2.0	2.16
	5 Mev. electrons		
Hopkins (1951)	5.3 Mev. electrons	11.6	10.8
	5.3 Mev. α -particles		

Although the present discussion has been confined to anthracene, for which most experimental data are available, the response curves for other organic crystals to different ionizing particles will be very similar. It is known that the ratio of the response to 5-mev. α -particles and electrons is approximately the same for anthracene, naphthalene (Birks 1950 a) and terphenyl (Hofstadter 1950), and similar results are to be expected for stilbene, phenanthrene, dibenzyl and the other fluorescent hydrocarbons.

REFERENCES

- BETHE, H. A., 1950, *Rev. Mod. Phys.*, **22**, 213.
 BIRKS, J. B., 1950 a, *Proc. Phys. Soc. A*, **63**, 1294; 1950 b, *Ibid.*, **63**, 1044.
 BIRKS, J. B., and BLACK, F. A., 1951, *Proc. Phys. Soc. A*, **64**, 511.
 BOWEN, E. J., MIKIEWICZ, E., and SMITH, F. W., 1949, *Proc. Phys. Soc. A*, **62**, 26.
 CURIE, Mme. P., 1935, *Radioactivité* (Paris: Hermann).
 FRANZEN, W., PELLE, R. W., and SCHERR, R., 1950, *Phys. Rev.*, **79**, 742.
 HARDING, G. N., FLOWERS, B. H., and EPPSTEIN, J. S., 1949, *Nature, Lond.*, **163**, 990.
 HOFSTADTER, R., 1950, *Nucleonics*, **6**, No. 5, 72.
 HOPKINS, J. I., 1951, *Rev. Sci. Instrum.*, **22**, 29.
 LIVINGSTON, M. S., and BETHE, H. A., 1937, *Rev. Mod. Phys.*, **9**, 245.

Effect of the Change in Lattice Parameter on the Width of the Forbidden Energy Zone according to Kronig and Penney's One-Dimensional Lattice Model

By E. BILLIG

Associated Electrical Industries Ltd., Aldermaston, Berks.

MS. received 8th March 1951, and in amended form 17th May 1951

ABSTRACT. The effect of changing the lattice parameter in Kronig and Penney's linear lattice model is investigated theoretically. Möglich and Rompe have predicted a decrease in the width of the forbidden energy zone as the lattice parameter is increased. It is shown that this is true only if the width of the potential troughs is increased whilst the thickness of the barriers is maintained constant. However, the opposite effect, i.e. an increase in the width of the forbidden zone, is expected when the potential troughs are kept constant and the width of the barriers is increased instead. In the intermediate case of a uniform expansion of potential hills and troughs, a small net decrease in the width of the forbidden zone is expected.

THE effects of various factors on the electrical and optical properties of intrinsic semiconductors have recently been investigated experimentally and efforts are being made to account for them on the current band theory of solids. Changes in temperature and pressure have been found to affect the fundamental lattice absorption (optical branch) and particularly the intrinsic conductivity of semiconductors. The long-wave edge of the optical or ultra-violet absorption band of many insulators is shifted towards the red as the temperature is increased (by about $1\text{ Å}/^\circ\text{C.}$) and conversely towards the blue on the application of a high pressure, (in CdS crystals for instance by about 0.02 Å/atm. (Höhler 1949)).

One cause of these effects is the change in inter-atomic distances produced by thermal expansion or by mechanical compression. This change in lattice parameter has been considered by Möglich and Rompe (1942) in an effort to calculate the magnitude of the temperature effect. Using the well-known linear model of Kronig and Penney (1931), they arrive at the conclusion that the width of the forbidden energy band which determines the absorption edge decreases as the lattice parameter is increased, the percentage decrease being equal to twice the percentage increase in lattice parameter. This result seems rather surprising; it might be expected that at large inter-atomic distances such a lattice would behave as an insulator with discrete energy levels and that, as the atoms are brought more closely together, these levels would gradually broaden into bands, i.e. that the energy gap would gradually be reduced. It is the purpose of this note to re-examine the problem, as Möglich and Rompe's conclusions continue to be used by subsequent investigators (Höhler 1949, Seiwert 1949).

It will be recalled that Kronig's model consisted of the periodic arrangement in one dimension of potential troughs (of width a and potential $V=0$), alternating with potential barriers (of width b and height V_0) corresponding to the barriers which impede the free passage of electrons from one atom to the next. Solution of Schrödinger's equation with these boundary conditions yielded the following relation for the permitted energy levels (eigenvalues W) of the electron :

$$\frac{\gamma^2 - \beta^2}{2\beta\gamma} \sinh \gamma b \sin \beta a + \cosh \gamma b \cos \beta a = \cos \alpha (a+b), \quad \dots\dots (1)$$

where the wave vector $\beta = CW^{1/2}$, and $\gamma = C(V_0 - W)^{1/2}$, $C^2 = 8\pi^2 m/h^2$, and α could assume any real value. Equation (1) yielded real values of W only for certain ranges of α : only if the absolute value of the expression on the left does not exceed unity does the solution correspond to a permitted (real) energy value and the electrons are in an allowed band; the alternative of imaginary energy values corresponds to electrons in a forbidden zone. Kronig and Penney discussed their solution under the following two simplifying assumptions: (i) $\beta \ll \gamma$, i.e. the discussion is restricted to those energy values of the electrons which are well below the top of the barrier ($W \ll V_0$); transition of electrons occurs by tunnelling through the potential barrier rather than by passing over it. (ii) $b\gamma \ll 1$, i.e. the value of the parameter $P \equiv \gamma^2 ab/2 = V_0 b a C^2/2$, which is proportional to the product of barrier height and width (the 'barrier resistance'), remains finite.

Under these assumptions, equation (1) reduced to

$$(P \sin \beta a)/\beta a + \cos \beta a = \cos \alpha a. \quad \dots\dots(2)$$

We are here interested in insulators and intrinsic semiconductors, particularly in the energy values corresponding to the upper edge of the first (full) band and the lower edge of the second (empty) band, their difference corresponding to the width of the forbidden zone. At these edges the right-hand sides of equations (1) and (2) assume the extreme values ± 1 . Equation (2) is then fulfilled if either $\beta_1 a = \pi$, corresponding to the top of the first (full) band, or if

$$\beta_2 a \cot(\beta_2 a/2) = -P, \quad \dots\dots(3)$$

corresponding to the bottom of the second (empty) band, the difference in the respective energy levels, $W = \beta^2/C^2$, determining the width of the forbidden gap W_g .

The effect of altering the width of the potential trough a is found by differentiating W_g with respect to a , whilst maintaining the barrier height V_0 and width b , i.e. the barrier resistance, constant. This always results in a negative value, $dW_g/da < 0$ (Figure 1(b)); as the space available to an electron between two adjacent barriers is increased, so the forbidden band becomes narrower, the model assumes a more and more metallic character. This is essentially Möglich and Rompe's result, except that their actual formula considerably over-estimates the change in gap width.*

Instead of maintaining b constant and varying a , we might keep a constant and vary b . This can be done whilst still maintaining the useful approximations $\beta \ll \gamma$ and $b\gamma \ll 1$.† The gap is then found to *increase* with increasing b (Figure 1(c)); as the barrier becomes wider, the probability of an electron tunnelling across decreases and the situation in the limit of large separation approaches the case of tight binding, i.e. of discrete energy levels.

The intermediate case of uniform strain along the lattice, $\delta a/a = \delta b/b$, leads to the width of the gap always decreasing with increasing lattice parameter, as in the case considered first, but the decrease is considerably less.

In conclusion, expansion of the lattice may, according to this model, lead to either a narrowing or a widening of the forbidden zone, the former if the width of the troughs is increased and the latter if the width of the potential barriers is

* Möglich and Rompe have not allowed for the variation of the cotangent term when in effect differentiating equation (3).

† The barrier resistance ($V_0 b$ or P) does not, of course, remain constant in this case.

increased. It cannot easily be decided which alternative is the correct one; Kronig and Penney's model is in fact too simple to be used for quantitative calculations as it does not take into account any finer details of the atoms making up the lattice. More quantitative results are obtained by using the appropriate atomic or ionic potential functions instead of square barriers. A good approximation for the proper wave function is obtained by a linear combination of the atomic orbitals of lowest energy (l.c.a.o. method) in such a way that continuity of the wave function and of its first derivative is maintained when going from any one atom to its nearest neighbour (Wigner and Seitz 1933). This treatment is equally suitable for one-, two- or three-dimensional lattices and yields detailed results for the electronic band structure of metallic or covalent solids which can be used for comparison with experiment. The result of such a calculation for diamond is shown in Figure 1(a), giving the energy bands as a function of inter-nuclear

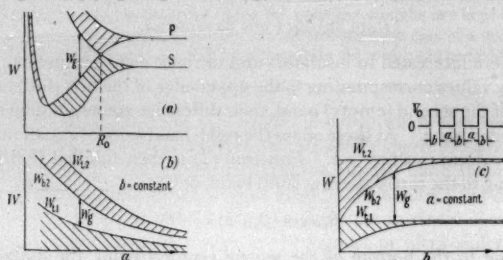


Figure 1. Electronic band structure of covalent solids: (a) l.c.a.o. method (Kimball 1935); (b) square barriers of constant thickness b ; (c) square barriers between potential troughs of constant width a .

distance (Kimball 1935). It is interesting to note that according to this structure also—which is typical for many solids—either an increase or a decrease in gap width may arise on expansion of the lattice. For the covalent lattices calculated so far (C, Si) the equilibrium distance is less than the spacing corresponding to the crossover point, R_0 . Theory thus predicts a decrease of the energy gap with expansion of these lattices, in agreement with experiment.

ACKNOWLEDGMENT

Thanks are due to Dr. T. E. Allibone for permission to publish this paper.

REFERENCES

- HÖHLER, G., 1949, *Ann. Phys., Lpz.*, **4**, 371.
- KIMBALL, G. E., 1935, *J. Chem. Phys.*, **3**, 560.
- KRONIG, R. L., and PENNEY, W. G., 1931, *Proc. Roy. Soc. A*, **130**, 499.
- MÖGLICH, F., and ROMPE, R., 1942, *Z. Phys.*, **119**, 472.
- SEIWER, R., 1949, *Ann. Phys., Lpz.*, **6**, 241.
- WIGNER, E., and SEITZ, F., 1933, *Phys. Rev.*, **43**, 804.

Influence of a Black Sphere and of a Black Cylinder upon the Neutron Density in an Infinite Non-Capturing Medium

By B. DAVISON

Atomic Energy Research Establishment, Harwell, Didcot, Berks.

Communicated by R. E. Peierls; MS. received 12th April 1951

ABSTRACT. For a black body inserted into a homogeneous scattering medium, the neutron density at large distances from the body is determined using the perturbation method for the case when the scattering in the scattering medium is assumed elastic and isotropic capture is absent and the following four types of the black body are considered: (i) a sphere of radius small compared with the mean free path in the scattering medium; (ii) a sphere of radius large compared with the mean free path; (iii) an infinitely long cylinder of radius small compared with the mean free path; (iv) an infinitely long cylinder of radius large compared with the mean free path. Combining the results for the above limiting cases with the results obtained by other methods the distribution is also estimated for a sphere and an infinitely long cylinder of intermediate radii.

INTRODUCTION

THE integral equation for the neutron density in a non-capturing isotropically scattering medium occupying a convex volume V , in the presence of black bodies inside this volume, is (Peierls 1939)

$$n(r) = \frac{1}{4\pi} \iiint_{V'(r)} \frac{n(r')}{R^2} e^{-R} dV_{r'} + n_0(r), \quad \dots\dots(1)$$

provided that we are dealing with the stationary case and that the mean free path of the neutrons is independent of energy. Here all distances are measured in units of mean free path, R is the distance between r and r' , $V'(r)$ is the part of the volume V which is not shielded from r by the black bodies and $n(r)$ is the neutron track length per unit volume per unit time in the vicinity of r . For brevity we shall refer to $n(r)$ as the neutron density, though the use of this latter term is not truly justifiable, unless we assume that neutrons are scattered without change in energy. $n_0(r)$ is the contribution to $n(r)$ due to neutrons which have come directly from the sources or directly from outside the volume V , without having been scattered in V .

It is known that in the source free regions $n(r)$ can be presented in the following form†

$$n(r) = n_{\text{diff}}(r) + n^*(r) \quad \dots\dots(2)$$

in which $n_{\text{diff}}(r)$ satisfies the diffusion differential equation

$$\nabla^2 n_{\text{diff}}(r) = 0 \quad \dots\dots(3)$$

while $n^*(r)$ is of the order of $e^{-\delta}$, δ being the distance from the point r to the nearest source, or the nearest point on the outer boundary of V , or on the surface of the nearest black body, whichever is the smaller. If the dimensions of V and the distances of the black bodies from the outer surface of V and between each other are large, it is usually sufficient to know $n_{\text{diff}}(r)$ rather than $n(r)$ itself. Equation (3) is not sufficient in itself to determine $n_{\text{diff}}(r)$, one should know also the boundary

† This could be seen by slightly extending the analysis given by Bothe (1942).

conditions satisfied by the latter at the boundaries of the regions containing sources, at the outer boundary of the volume V and at the surfaces of the black bodies. In the present paper we shall be concerned only with the boundary conditions at the surface of a black body. To specify these boundary conditions it is sufficient to determine the ratio

$$n_{\text{diff}}(r) / \frac{\partial n_{\text{diff}}(r)}{\partial \nu} \dots\dots (4)$$

(in which ν is the direction of the outer normal) at the surface of the black body. If the black body is situated at a large distance from all sources, other black bodies and the outer boundary of the volume V , then the values of (4) should depend almost entirely upon the size and shape of our black body.

We can determine an approximate value of (4) by solving the idealized problem in which the scattering medium extends to infinity in all directions, containing no other black bodies apart from the one for which we wish to determine the boundary conditions, and the neutrons are assumed to be supplied from infinity uniformly from all directions. In this idealized problem $n_{\text{diff}}(r)$ gives, at the same time, the asymptotic behaviour of $n(r)$ at large distances from the black body, and accordingly we shall denote it henceforth as $n_{\text{as}}(r)$. The value of the quantity (4) can be referred to as the linear extrapolation length, we shall denote it by λ .

The values of λ for a sphere have been calculated by Marshak (1947 a, b) for a wide range of values of the radius using numerical approximation methods. It has also been shown by Placzek (private communication) that for a convex black body of a fixed shape λ should tend to the value $4/3$ as the size of the black body tends to zero, while as the size of the black body becomes infinite the problem becomes the Milne one, for which $\lambda = 0.7104$ (see, for example, Hopf 1934, p. 85). It has been conjectured further that λ varies monotonically with size of the black body. This suggests that one might try to determine expansions for λ , valid for small and large sizes. These expansions are of interest also for the spherical case, despite Marshak's work. For a small sphere, in particular, the spherical harmonics method breaks down while the other method used by Marshak requires extremely laborious numerical work, but if use has to be made of expansions it is of course preferable to have an expansion of the correct function rather than that of an approximate one as obtained by Marshak.

In the present paper we shall limit ourselves to the determination of the first few terms of these expansions for the spherical and the cylindrical cases. We shall consider the cases of large and small black spheres, and of an infinitely long black cylinder of large radius in Parts I, II and III of this paper respectively. The case of a black cylinder infinitely long and of small radius has been considered by Kushneriuk (1951) following essentially the same method as in Parts I to III of the present paper. For the sake of completeness we include, in the beginning of Part IV, a short summary of Kushneriuk's article.

In all cases we shall denote by r the radial coordinate and by a the radius of the black body, both expressed of course in units of the mean free path of the external medium. With these notations the expression (4) becomes

$$\lambda = n_{\text{as}}(a) / n'_{\text{as}}(a) \dots\dots (4')$$

For a large sphere and a large cylinder we shall determine λ to the accuracy of $O(a^{-3})$, i.e. we include terms of the order of a^{-3} , but omit terms of the order of

$a^{-4} \log a$. For a small sphere we shall determine λ to the accuracy of $O(a^2)$ and for a small cylinder to the accuracy of $O(a)$. The method of calculation used is essentially that of successive approximations, but the detailed arrangement of the successive approximations is different in each case. However in all cases, in order to avoid working out the terms which finally give no contribution within the accuracy intended, we start by examining the order of magnitude of various expressions arising in the application of the successive approximations method. Due to the limitations of space we shall give only a short account of some of the stages of the calculation while for the complete details the reader is referred to the original declassified reports.*

In the second half of Part IV we give the complete curves of $\lambda(a)$ for the spherical and the cylindrical cases, obtained by combining the results of the calculations given in Parts I to IV and those for the intermediate values of a by means of the spherical harmonics method.

Throughout this paper we use the notations

$$E_n(x) = \int_1^\infty e^{-xt} t^{-n} dt; \quad E(x) = E_1(x) \quad \dots\dots(5)$$

Euler's constant $\gamma = 0.57722$ and $\delta(x)$ is Dirac's δ -function. The symbols q , q_n and f_n will have different meanings in each of the four parts of this paper.

PART I

CASE OF A LARGE BLACK SPHERE

§1. METHOD OF THE SOLUTION

In this case, on integration over angles the equation (1) reduces to

$$rn(r) = \frac{1}{2} \int_a^\infty r'n(r') [E(|r-r'|) - E\{(r^2-a^2)^{1/2} + (r'^2-a^2)^{1/2}\}] dr'. \quad \dots\dots(1.1)$$

If we put $r = a + x$, $r' = a + y$, $rn(r) = q(x)n(\infty)$ (1.2)
it becomes

$$q(x) = \frac{1}{2} \int_0^\infty q(y) E(|x-y|) dy - \frac{1}{2} \int_0^\infty q(y) E\{(x^2+2ax)^{1/2} + (y^2+2ay)^{1/2}\} dy, \quad \dots\dots(1.3)$$

with $q(x)$ normalized so that $q'(\infty) = 1$, while the expression for $n_{as}(r)$ can obviously be put into the form $n_{as}(r) = r^{-1}[r-a + \{q(x)-x\}|_{x=\infty}]n(\infty)$ (notice that according to (2) and (3) $q(x)$ behaves for large x as x), and hence from (4')

$$\lambda = \frac{\{q(x)-x\}|_{x=\infty}}{1-a^{-1}\{q(x)-x\}|_{x=\infty}}. \quad \dots\dots(1.4)$$

To solve the equation (1.3), put $q(x) = q_0(x) + q_1(x) + \dots\dots$ in which $q_0(x)$ and $q_n(x)$ ($n \geq 1$) are the solutions of the equations

$$\left. \begin{aligned} q_0(x) &= \frac{1}{2} \int_0^\infty q_0(y) E(|x-y|) dy \\ q_n(x) &= \frac{1}{2} \int_0^\infty q_n(y) E(|x-y|) dy + f_n(x) \quad (n \geq 1) \end{aligned} \right\} \quad \dots\dots(1.5)$$

satisfying the conditions at ∞ , $q_0'(\infty) = 1$ $q_n'(\infty) = 0$ ($n \geq 1$).(1.6)

* Davison (1944, 1945); Seidel, Davison and Kushneriuk (1946). During preparation of this paper for publication a minor algebraic mistake has been discovered in Davison (1945). This is now corrected.

Here
$$f_n(x) = -\frac{1}{2} \int_0^\infty q_{n-1}(y) E\{(x^2 + 2ax)^{1/2} + (y^2 + 2ay)^{1/2}\} dy. \quad \dots\dots(1.7)$$

The function $q_0(x)$ is, of course, the solution of the Milne problem, and it has been already extensively studied. In particular it is known that

$$x < q_0(x) < x + 0.7104 \dots, \text{ and that } \lim_{x \rightarrow \infty} \{q_0(x) - x\} = 0.7104 \dots *$$

§ 2. LEMMA

In determining other $q_n(x)$ it is convenient to introduce an auxiliary function $q(x, x_0)$ defined as the solution of the equation

$$q(x, x_0) = \frac{1}{2} \int_0^\infty q(y, x_0) E(|x - y|) dy + \delta(x_0 - x) \quad \dots\dots(1.8)$$

satisfying the condition at ∞ :
$$\left[\frac{\partial}{\partial x} q(x, x_0) \right]_{x=\infty} = 0 \quad (x_0 \text{ finite}). \quad \dots\dots(1.9)$$

Then $q_n(x)$ for $n \geq 1$ will be given by

$$q_n(x) = \int_0^\infty f_n(x_0) q(x, x_0) dx_0. \quad \dots\dots(1.10)$$

The function $q(x, x_0)$ can be interpreted, except at $x = x_0$, as the neutron density in a half-space at the distance x from the boundary, due to a plane source of unit strength situated at a distance x_0 inside the medium, satisfying the condition that for finite x_0 the neutron current at infinity is zero. Then according to the optical reciprocity theorem $q(x, x_0)$ should be symmetrical in x and x_0 . On the other hand if we make x_0 tend to infinity $q(x, x_0)$ will obviously in the limit go over into the solution of the Milne problem, i.e. $q(x, \infty)$ is proportional to $q_0(x)$. But while $q(x, \infty)$ is normalized to unit current $q_0(x)$ is normalized to a value equal to $\frac{1}{3}$ at infinity. Collecting these results we see that $q(\infty, x) = q(x, \infty) = 3 q_0(x)$ and hence the asymptotic behaviour of $q_n(x)$ for large x , which alone will be needed in the final answer (1.4), according to (1.10) is given by

$$q_n(\infty) = 3 \int_0^\infty f_n(x) q_0(x) dx. \quad \dots\dots(1.11)$$

§ 3. ORDER OF MAGNITUDE OF SUCCESSIVE CORRECTIONS

Let us estimate now the order of magnitude of various $q_n(x)$, $f_n(x)$ and $q_n(\infty)$.

Let us assume that $|q_{n-1}(x)| \leq A_{n-1} + B_{n-1}x. \quad \dots\dots(1.12)$

(This is known to be correct for $q_0(x)$ with $A_0 = 0.7104 \dots$ and $B_0 = 1$.) Then one can easily derive from (1.7)

$$\begin{aligned} |f_n(x)| &< \frac{1}{2a} A_{n-1} E_3(x^2 + 2ax)^{1/2} \\ &+ \frac{3}{2a^2} B_{n-1} E_3(x^2 + 2ax)^{1/2} < \left[\frac{1}{a} A_{n-1} + \frac{3}{a^2} B_{n-1} \right] \frac{1}{2} E_3(x). \quad \dots\dots(1.13) \end{aligned}$$

On the other hand, it is known that by increasing the free term in the inhomogeneous equation (1.5) we shall necessarily increase the bounded solution (Hopf 1934, p. 36). But if the free term is equal to $[a^{-1} A_{n-1} + 3a^{-2} B_{n-1}] \frac{1}{2} E_3(x)$ the

* Hopf, (1934) pp. 28 ff. and pp. 47 ff. Notice that our $q_0(x)$ corresponds to Hopf's $\pi + q(x)$.

bounded solution is known to be equal to $[a^{-1} A_{n-1} + 3a^{-2} B_{n-1}] \{q_0(x) - x\}$, in which the second factor cannot exceed 0.7104.... Thus

$$|q_n(x)| < 0.7104 \dots [a^{-1} A_{n-1} + 3a^{-2} B_{n-1}],$$

i.e. (1.12) is valid for any n provided we take for $n \geq 1$

$$A_n = (0.7104 \dots a^{-1})^n (0.7104 + 3a^{-1}); B_n = 0. \dots (1.14)$$

This shows that our process of successive approximations converges for all a greater than 0.7104.... Using (1.13) one can show further that, if A' and B' are some positive numbers,

$$\left| \int_0^\infty (A' + xB') f_n(x) dx \right| \leq \frac{A_{n-1}A'}{8a^2} + \frac{3B_{n-1}A' + 4A_{n-1}B'}{16a^3} + \frac{9B_{n-1}B'}{16a^4}.$$

Combining this with (1.11) and (1.14) we see at once that

$$q_n(\infty) = O(a^{-n-1}). \dots (1.15)$$

In a similar manner one can also show that if in working out $q_{n-1}(x)$ we neglect a term of the order of $C(a)x^m(\log x)^k$ the resulting error in evaluating $q_n(x)$ is of the order of $C(a)a^{-m}(\log a)^k$ while the error in evaluating $q_n(\infty)$ will be of the order of $C(a)a^{-m-1}(\log a)^k$.

Comparison of the order of magnitude of $q_n(\infty)$ and of $q_n(x)$ for unrestricted x , suggests that the part of $q_n(x)$ which is of $O(a^{-n})$, $n \geq 1$, should come entirely from the free term of the equation (1.5) while the iterated term should be of a higher order of smallness. In fact one can easily show (see Appendix A) that

$$|q_n(x) - f_n(x)| = O(a^{-n-1} \log a) + a^{-n} O(x \log x) (n \geq 1). \dots (1.16)$$

Then, if in working out $q_{n+1}(\infty)$ we replace, in the definition of $f_{n+1}(x)$, $q_n(y)$ by $f_n(y)$, the resulting error, according to the previous remark, will be of the order of $a^{-n-2} \log a$.

Estimating in this manner we obtain in particular

$$\{q(x) - x\}|_{x=\infty} = \{q_0(x) - x\}|_{x=\infty} + q_1(\infty) + \tilde{q}_2(\infty) + O(a^{-4} \log a) \dots (1.17)$$

in which $\tilde{q}_2(\infty)$ is the expression obtained from the expression for $q_2(\infty)$ by replacing $q_1(y)$ by $f_1(y)$.

§ 4. EVALUATION OF INTEGRALS INVOLVED IN SECOND AND THIRD APPROXIMATIONS

Now, combining (1.7) and (1.11) we have

$$\begin{aligned} q_1(\infty) &= -\frac{3}{2} \int_0^\infty \int_0^\infty q_0(x) q_0(y) E\{(x^2 + 2ax)^{1/2} + (y^2 + 2ay)^{1/2}\} dx dy \\ \tilde{q}_2(\infty) &= \frac{3}{4} \int_0^\infty \int_0^\infty \int_0^\infty q_0(x) q_0(z) E\{(x^2 + 2ax)^{1/2} + (y^2 + 2ay)^{1/2}\} E\{(y^2 + 2ay)^{1/2} \\ &\quad + (z^2 + 2az)^{1/2}\} dx dy dz. \dots (1.18) \end{aligned}$$

To evaluate the integrals (1.18) for large a we need the expansion of $q_0(x)$ for small x . The derivation of this expansion from Hopf's solution for $q_0(x)$ is straightforward though laborious. It has been carried out by Mark (1944), who obtained the following result:

$$q_0(x) = \frac{1}{\sqrt{3}} \{1 - \frac{1}{2}x \log x + c_1 x + O(x^2 \log^2 x)\}, \dots (1.19)$$

in which $c_1 = 1.278794$. Substituting this into the expression for $q_1(\infty)$ we get

$$q_1(\infty) = -\frac{1}{2} \int_0^\infty \int_0^\infty E\{(x^2 + 2ax)^{1/2} + (y^2 + 2ay)^{1/2}\} dx dy \\ - \int_0^\infty \int_0^\infty x(-\frac{1}{2} \log x + c_1) E\{(x^2 + 2ax)^{1/2} + (y^2 + 2ay)^{1/2}\} dx dy + O(a^{-4} \log^2 a). \quad \dots\dots(1.20)$$

Making the substitutions $s = (x^2 + 2ax)^{1/2}$, $t = (y^2 + 2ay)^{1/2}$ we can easily see that the first term in (1.20) becomes

$$-\frac{1}{2} \int_0^\infty \int_0^\infty E(s+t) \frac{s ds}{(s^2 + a^2)^{1/2}} \frac{t dt}{(t^2 + a^2)^{1/2}} = -\frac{1}{2a^2} \int_0^\infty \int_0^\infty st E(s+t) ds dt + O(a^{-4}) \\ = -\frac{1}{8a^2} + O(a^{-4}). \quad \dots\dots(1.21)$$

Similarly, the second term in (1.20) gives $-(1/4a^3)(\log 2a + 2c_1 + 2\gamma - 10/3) + O(a^{-5} \log a)$, while for $\tilde{q}_2(\infty)$ we obtain the expression

$$\tilde{q}_2(\infty) = \frac{1}{4a^3} \int_0^\infty \int_0^\infty \int_0^\infty stu E(s+u) E(u+t) ds du dt + O(a^{-4} \log a) \\ = \frac{1}{4a^3} (\log 2 - \frac{2}{3}) + O(a^{-4} \log a).$$

§ 5. RESULTS

Substituting the above into (1.17) we obtain

$$\{q(x) - x\}|_{x=\infty} = 0.7104 \dots - \frac{1}{8a^2} - \frac{\log a}{4a^3} - \frac{1}{2a^3} (c_1 + \gamma - \frac{4}{3}) + O(a^{-4} \log a),$$

while substituting the last expression into (1.4), expanding in powers of a^{-1} and using the numerical values of c_1 and γ quoted above, we finally obtain

$$\lambda = 0.7104 \dots + 0.5047 a^{-1} + 0.2336 a^{-2} - \frac{1}{4} a^{-3} \log a - 0.1704 a^{-3} - O(a^{-4} \log^2 a). \quad \dots\dots(1.22)$$

It should be pointed out that while the series $q(x) = q_0(x) + q_1(x) + \dots$ is, as we have seen, absolutely convergent for all a greater than $0.7104 \dots$, the series obtained by expanding (1.22) will, presumably, be only asymptotically convergent since, for instance, the expansion of

$$\int_0^\infty \int_0^\infty E\{(x^2 + 2ax)^{1/2} + (y^2 + 2ay)^{1/2}\} dx dy$$

in powers of a^{-1} (see (1.21)) is only asymptotically convergent.

PART II

CASE OF SMALL BLACK SPHERE

§ 1. GENERAL OUTLINE OF THE METHOD AND EXAMINATION OF CONVERGENCE

We start, as in the preceding case, with the equation (1.1). However, instead of (1.2) we shall put

$$n(r) = r^{-1} n(\infty) \{r + q(r)\} \quad \dots\dots(2.1)$$

so that the equation (1.1) gives

$$q(r) = \frac{1}{2} \int_a^\infty q(t) [E(|r-t|) - E\{(r^2 - a^2)^{1/2} + (t^2 - a^2)^{1/2}\}] dt + \epsilon_3(r, a) \quad (r \geq a) \quad \dots\dots(2.2)$$

in which $\epsilon_3(r, a) = \frac{1}{2}\{E_3(r-a) - E_3(r^2 - a^2)^{1/2} - aE_2(r-a)\}$ ($r \geq a$) (2.3)

and $q(r)$ is that solution of equation (2.2) which is bounded at infinity. Notice that our present $q(r)$ and $\epsilon_3(r, a)$ are identical, except for the sign, with Marshak's $Q(r)$ and $\epsilon_3(r)$ (Marshak 1947 a).

$n_{as}(r)$ will obviously be given by $n_{as}(r) = r^{-1}n(\infty)[r + q(\infty)]$ and hence, from (4),

$$\lambda = -a^2/q(\infty) - a. \quad \dots\dots (2.4)$$

Turn now to the solution of equation (2.2) for small a . This can be done by means of the perturbation method. In order to apply this method, it will be convenient to extend the definition of $q(r)$ and $\epsilon_3(r, a)$, for the region $0 \leq r < a$. This we shall do by putting there

$$\left. \begin{aligned} q(r) &= \frac{1}{2} \int_a^\infty dt q(t) \{E(|r-t|) - E(r+t)\} & (0 \leq r < a), \\ \epsilon_3(r, a) &= 0 & (0 \leq r < a). \end{aligned} \right\} \quad \dots\dots (2.5)$$

For brevity we shall write

$$\left. \begin{aligned} \Lambda\phi(r) &= \frac{1}{2} \int_0^\infty dt \phi(t) \{E(|r-t|) - E(r+t)\}, \\ \Delta_1\phi(r) &= \frac{1}{2} \int_0^a dt \phi(t) \{E(|r-t|) - E(r+t)\}, \\ \Delta_2\phi(r) &= \begin{cases} \frac{1}{2} \int_a^\infty dt \phi(t) [E((r^2 - a^2)^{1/2} + (t^2 - a^2)^{1/2}) - E(r+t)] & \text{for } r \geq a, \\ 0 & \text{for } 0 \leq r < a. \end{cases} \end{aligned} \right\} \quad \dots\dots (2.6)$$

Then the equation (2.2) can be re-written in the form

$$q(r) = \Lambda q(r) - (\Delta_1 + \Delta_2) q(r) + \epsilon_3(r, a). \quad \dots\dots (2.7)$$

Put now $q(r) = q_0(r) + q_1(r) + \dots\dots$ (2.8)

in which $q_n(r)$ is the solution, bounded for $r \rightarrow \infty$, of the equation

$$(1 - \Lambda)q_n(r) = f_n(r) \quad (n = 0, 1, 2, \dots) \quad \dots\dots (2.9)$$

in which $f_0(r) = \epsilon_3(r, a)$, $f_n(r) = -(\Delta_1 + \Delta_2)q_{n-1}(r)$ ($n \geq 1$). (2.10)

One can easily establish that, for $r \gg a$,

$$\left. \begin{aligned} \epsilon_3(r, a) &= O(a^2 e^{-r}); \Delta_1\phi(r) = \text{Max} |\phi(r)| O(a^2 e^{-r}), \\ \Delta_2\phi(r) &= \text{Max} |\phi(r)| O(a^2 e^{-r}), \end{aligned} \right\} \quad \dots\dots (2.11)$$

while for r comparable with a , or $r \ll a$,

$$\epsilon_3(r, a) = O(a); \Delta_1\phi(r) = \text{Max} |\phi(r)| O(a), \Delta_2\phi(r) = \text{Max} |\phi(r)| O(a), \quad \dots\dots (2.11')$$

in which $\phi(r)$ is any function for which the operators Δ_1 and Δ_2 exist.

Now, since the kernel of the equations (2.9) is independent of a , $\text{Max} |q_n(r)|$ should be obviously of the same order of magnitude as $\text{Max} |f_n(r)|$. Then according to (2.10) and (2.11') $q_0(r) = O(a)$, $q_1(r) = O(a^2)$ and so on. Hence it follows that the series (2.8) will, for sufficiently small a , converge and its sum will be the solution of (2.7).

The solution of each of the equations (2.9) can be obtained, for instance, in the following way: $[q_n(r) - f_n(r)]$ can be regarded as r times the neutron density in an infinite (isotropically) scattering medium (occupying the entire space, i.e. in the absence of any black bodies) due to a spherically symmetrical system of distributed sources, the source density at the distance r being $f_n(r)/r$. Then if $p(r)$ is the neutron density due to a point source of unit strength in an infinite (isotropically) scattering medium in the absence of black bodies, $q_n(r)$ will obviously be given by

$$q_n(r) = \iiint \frac{r}{r_0} p(|r - r_0|) f_n(r_0) dr_0 + f_n(r), \quad \dots (2.12)$$

and $p(r)$ entering into (2.12) is already known (Bothe 1942).

§ 2. SIMPLIFICATION OF CALCULATIONS

The problem of determining λ to any prescribed accuracy for small a is thus reduced to the evaluation of certain multiple integrals. We shall consider now how to minimize the complexity of these integrals. If we wish to determine λ to the accuracy of $O(a^2)$ then, in view of (2.4), and since $q(\infty)$, as we shall see later, is $O(a^2)$, $q(\infty)$ should be determined to the accuracy of $O(a^4)$.

It has been shown by Marshak* that

$$q(\infty) = -\frac{3a^2}{4} + 3 \int_a^\infty q(r) \epsilon_3(r, a) dr$$

combining this with (2.7) we have

$$q(\infty) = -\frac{3a^2}{4} + 3 \int_a^\infty [\epsilon_3(r, a)]^2 dr - 3 \int_a^\infty \epsilon_3(r, a) (\Delta_1 + \Delta_2) q(r) dr + 3 \int_a^\infty \epsilon_3(r, a) \Lambda q(r) dr. \quad \dots (2.13)$$

It follows from the estimates (2.11) and (2.11') that the second term in (2.13) is of $O(a^3)$ and the third term is of $O(a^4)$. Let us now show that, provided we refer to the quantities of $O(a^m \log^k a)$ simply as $O(a^m)$, the fourth term in (2.13) is also of the order of a^4 .

We estimate first $\Lambda f_n(r)$. Using (2.10), (2.11) and (2.11') and understanding $O(a^m)$ in the sense explained above we can easily derive

$$\Lambda f_n(r) = O(a^{n+2}) \quad (\text{for any value of } r). \quad \dots (2.14)$$

On the other hand applying the operator Λ to (2.9) we obtain $(1 - \Lambda) \Lambda q_n(r) = \Lambda f_n(r)$, and hence by the argument already used before $\text{Max} |\Lambda q_n(r)|$ should be of the same order of magnitude as $\text{Max} |\Lambda f_n(r)|$. Using (2.14) then

$$\Lambda q_n(r) = O(a^{n+2}) \quad (\text{for any value of } r) \quad \dots (2.15)$$

while, combining this with the estimate of the order of magnitude of $\epsilon_3(r, a)$, we see, in fact, that that last term in (2.13) is of the order a^4 . If we are working out $q(\infty)$ to the accuracy of $O(a^4)$ this means that we shall need only the leading terms in the third and the fourth integrals in (2.13), and consequently we can replace $q(r)$ there by $q_0(r)$. Further it follows from (2.15) that $(\Delta_1 + \Delta_2) \Lambda q_0(r)$ is of a higher order of smallness than $(\Delta_1 + \Delta_2) \epsilon_3(r, a)$ and because $q_0(r) = \Lambda q_0(r) + \epsilon_3(r, a)$ we can replace the third term by

$$-3 \int_a^\infty \epsilon_3(r, a) (\Delta_1 + \Delta_2) \epsilon_3(r, a) dr + O(a^5). \quad \dots (2.16)$$

* See Marshak (1947 a) formula (23) bearing in mind that our $q(r)$ and $\epsilon_3(r, a)$ differ from his $Q(r)$ and $\epsilon_3(r)$ by the sign.

Let us now consider the last term. We will first approximate the expression for $q_0(r)$, so as to avoid the evaluation of the rather unwieldy integral (2.12). Let us start by obtaining an approximate expression for $f_0(r)$, i.e. for $\epsilon_3(r, a)$.

For $r \gg a$, expanding it into the powers of a and using the recurrence relationships between the functions $E_n(x)$ we obtain

$$\epsilon_3(r, a) = -\frac{a^2 e^{-r}}{4r} \left\{ 1 + O(a) + O\left(\frac{a^2}{r^2}\right) \right\} r \gg a. \quad \dots (2.17)$$

For r comparable with a the approximation (2.17) is no longer valid, the error becoming comparable with $\epsilon_3(r, a)$. However, the approximation (2.17) can be used to evaluate the leading term in $\Lambda \Lambda \epsilon_3(r, a)$ for any r . This can be seen as follows: According to the definitions (2.6)

$$\Lambda \left[\epsilon_3(r, a) + \frac{a^2 e^{-r}}{4r} \right] = \frac{1}{2} \int_0^\infty \left[\epsilon_3(t, a) + \frac{a^2 e^{-t}}{4t} \right] \{E(|r-t|) - E(r+t)\} dt. \quad \dots (2.18)$$

If $r \gg a$, then, for t comparable with a , $\{E(|r-t|) - E(r+t)\}$ is of the order t . Now $\{t \epsilon_3(t, a) + \frac{1}{4} a^2 e^{-t}\} = O(a^2)$ and the contribution from this range of t to the integral (2.18) is of the order a^3 , while for $t \gg a$ the integrand (according to (2.17)) is of the order a^3 . Thus for $r \gg a$ the integral (2.18) is of the order a^3 .

Similarly one can show that for r comparable with a , the integral (2.18) is of the order a^2 . Then, using a derivation similar to (2.14), one can show that for any value of r

$$\Lambda \Lambda \left[\epsilon_3(r, a) + \frac{a^2 e^{-r}}{4r} \right] = O(a^3). \quad \dots (2.19)$$

Remembering now that $p(r)$, which occurs in (2.12), satisfies the equation $(1-\Lambda)p(r) = e^{-r}/4\pi r$, we see that $(1-\Lambda)\Lambda[q_0(r) + \pi a^2 p(r)] = O(a^3)$ and hence, similarly to (2.15) $\Lambda[q_0(r) + \pi a^2 p(r)] = O(a^3)$, so that the last term in (2.13), on omitting the quantities of $O(a^5)$, can be re-written as

$$3 \int_a^\infty \epsilon_3(r, a) \Lambda \epsilon_3(r, a) dr - 3\pi a^2 \int_a^\infty \epsilon_3(r, a) \Lambda \Lambda p(r) dr + O(a^5). \quad \dots (2.20)$$

The last term in (2.20) can be transformed further. Substituting for Λ from (2.6) and changing the order of integration we have

$$-3\pi a^2 \int_0^\infty p(r) \Lambda \Lambda \epsilon_3(r, a) dr$$

which in view of (2.19), and omitting terms of $O(a^5)$ becomes

$$\frac{3\pi}{4} a^4 \int_0^\infty p(r) \Lambda \Lambda \frac{e^{-r}}{r} dr. \quad \dots (2.21)$$

Collecting the above results, and abandoning our convention of writing $O(a^m)$ instead of $O(a^m \log^k a)$ we obtain

$$\begin{aligned} q(\infty) = & -\frac{3a^2}{4} + 3 \int_a^\infty [\epsilon_3(r, a)]^2 dr + 3 \int_a^\infty \epsilon_3(r, a) (\Lambda - \Delta_1 - \Delta_2) \epsilon_3(r, a) dr \\ & + \frac{3\pi}{4} a^4 \int_0^\infty p(r) \Lambda \Lambda \frac{e^{-r}}{r} dr + O(a^5 \log^k a). \quad \dots (2.22) \end{aligned}$$

§ 3. EVALUATION OF THE INTEGRAL (2.21)

Now $p(r)$ is known only in terms of its Fourier transform: it has to be determined by the inversion formula, which would involve numerical integration. However, in order to evaluate the integral (2.21) we do not have to know $p(r)$ explicitly; it is sufficient to know its Fourier transform, if we make use of Plancherel's theorem (Titchmarsh 1937, p. 72). According to this theorem, if

$$A_s(u) = \sqrt{\frac{2}{\pi}} \int_0^\infty a(r) \sin ur \, dr \text{ and } B_s(u) = \sqrt{\frac{2}{\pi}} \int_0^\infty b(r) \sin ur \, dr$$

are the Fourier sine transforms of $a(r)$ and $b(r)$, then

$$\int_0^\infty a(r) b(r) \, dr = \int_0^\infty A_s(u) B_s(u) \, du.$$

Now the Fourier sine transform of e^{-r}/r is $(2/\pi)^{1/2} \tan^{-1} u$, while the Fourier sine transform of $\Lambda \phi(r)$ is equal to $u^{-1} \tan^{-1} u$ times the transform of $\phi(r)$. Then from the equation $(1-\Lambda)p(r) = e^{-r}/4\pi r$, it can be seen that the Fourier sine transform of $p(r)$ is $u \tan^{-1} u / (2\pi)^{3/2} (u - \tan^{-1} u)$, while the Fourier sine transform of $\Lambda \Lambda e^{-r}/r$ is $u(2/\pi)^{1/2} (u^{-1} \tan^{-1} u)^3$. Therefore integral (2.21) is equal to

$$\frac{3a^4}{8\pi} \int_0^\infty \frac{(\tan^{-1} u)^4 \, du}{u(u - \tan^{-1} u)}.$$

On making the substitution $\tan^{-1} u = \theta$, it becomes

$$\frac{3a^4}{8\pi} \int_0^{\pi/2} \frac{\theta^4 \, d\theta}{\sin \theta [\sin \theta - \theta \cos \theta]} \quad \dots\dots (2.23)$$

This last integral can be easily evaluated numerically, and the value of the expression (2.23) was found to be

$$0.72337a^4 \quad \dots\dots (2.23')$$

§ 4. EVALUATION OF THE OTHER INTEGRALS ENTERING (2.22)

To simplify the evaluation of the other integrals entering (2.22) it will be convenient to replace $\epsilon_3(r, a)$ by some approximation in terms of more elementary functions giving the desired accuracy for small values of a . To obtain such an approximation re-write the expression for $\epsilon_3(r, a)$ in the form

$$\epsilon_3(r, a) = \frac{e^{-r}}{4} \left[\exp a - \exp \{r - (r^2 - a^2)^{1/2}\} - (r^2 - a^2) \int_{r-a}^{(r^2 - a^2)^{1/2}} \frac{dt}{t^2} \exp(r-t) \right] \quad \dots\dots (2.24)$$

and expand $\exp a$, $\exp\{r - (r^2 - a^2)^{1/2}\}$ and $\exp(r-t)$ into powers of a , $\{r - (r^2 - a^2)^{1/2}\}$ and $(r-t)$ respectively, retaining the appropriate number of terms. Notice further that if we wish to evaluate

$$\int_a^\infty e^{-2r} F(r, a) \, dr,$$

say to an accuracy of $O(a^4 \log^k a)$, and if $F(r, a)$, for $r \gg a$, is of the order of a^5 we can, in this integral expand e^{-2r} into the powers of r and retain only the few first terms. In this manner one can show that

$$\begin{aligned} \int_a^\infty [\epsilon_3(r, a)]^2 \, dr &= \int_a^\infty \left\{ \frac{a^4 e^{-2r}}{16 r^2} + \frac{a^6 [3r + (r^2 - a^2)^{1/2}](1-2r)}{16 r^2 [r + (r^2 - a^2)^{1/2}]^3} \right. \\ &\quad \left. - \frac{a^2}{4[r + (r^2 - a^2)^{1/2}]} \left[\frac{r^2 - a^2}{2} \log \frac{r+a}{r-a} - ra - \frac{a^4}{[r + (r^2 - a^2)^{1/2}]^2} \right] \right\} dr + O(a^5 \log^k a). \end{aligned} \quad \dots\dots (2.25)$$

The integrals entering into the last expression, apart from the one leading to E -functions are either elementary or expressible in terms of the series

$$\sum_{n=1}^{\infty} 1/n^2 = \pi^2/6, \text{ and the ultimate result is*}$$

$$3 \int_a^{\infty} [\epsilon_3(r, a)]^2 dr = \frac{a^3}{4} + \frac{3}{8} a^4 \left[\log a + \gamma + \frac{3\pi^2}{16} - \frac{3}{2} \right] + O(a^5 \log^k a). \quad \dots (2.25')$$

Turn now to the integral $-\int_a^{\infty} \epsilon_3(r, a) (\Delta_1 + \Delta_2) \epsilon_3(r, a) dr$. Notice that, according to the definitions (2.5) and (2.6), $\Delta_1 \epsilon_3(r, a) = 0$. In evaluating

$$\int_a^{\infty} \epsilon_3(r, a) \Delta_2 \epsilon_3(r, a) dr$$

we can replace $\epsilon_3(r, a)$ by $-a^2/\{r + (r^2 - a^2)^{1/2}\} + O(a^2)$, on the grounds of (2.24), and similarly replace the function $[E\{r^2 - a^2\}^{1/2} + (t^2 - a^2)^{1/2} - E(r + t)]$ occurring in the definition of the operator Δ_2 by the leading term of its expansion for small r and t , i.e. by $\log(r + t)/\{(r^2 - a^2)^{1/2} + (t^2 - a^2)^{1/2}\}$. Thus, we have

$$\begin{aligned} & -3 \int_a^{\infty} \epsilon_3(r, a) (\Delta_1 + \Delta_2) \epsilon_3(r, a) dr \\ &= -\frac{3a^4}{8} \int_a^{\infty} \int_a^{\infty} \frac{dr}{r + (r^2 - a^2)^{1/2}} \frac{dt}{t + (t^2 - a^2)^{1/2}} \log \frac{r + t}{(r^2 - a^2)^{1/2} + (t^2 - a^2)^{1/2}} + O(a^5) \\ & \dots\dots (2.26) \end{aligned}$$

on evaluating the integral by means of series we get

$$-\frac{3a^4}{16} \left\{ \sum_{n=0}^{\infty} \frac{1}{(2n+1)^3} + \frac{5}{4} - \frac{3\pi^2}{16} \right\} + O(a^5). \quad \dots\dots (2.26')$$

Consider now the last remaining integral, i.e. $3 \int_a^{\infty} \epsilon_3(r, a) \Lambda \epsilon_3(r, a) dr$.

On the grounds of the considerations developed above it can be re-written as

$$\frac{3}{4} a^4 \int_a^{\infty} \int_a^{\infty} \frac{e^{-r-t} dr dt}{\{r + (r^2 - a^2)^{1/2}\} \{t + (t^2 - a^2)^{1/2}\}} \{E(|r - t|) - E(r + t)\} + O(a^5)$$

or alternatively as

$$\begin{aligned} & \frac{3}{8} a^4 \int_a^{\infty} \frac{e^{-r}}{r} \int_r^{\infty} \frac{e^{-t}}{t} [E(t - r) - E(t + r)] dt dr \\ & + \frac{3}{2} a^4 \int_a^{\infty} dr \int_r^{\infty} dt \left\{ \frac{1}{\{r + (r^2 - a^2)^{1/2}\} \{t + (t^2 - a^2)^{1/2}\}} - \frac{1}{4rt} \right\} \log \frac{t + r}{t - r} + O(a^5). \\ & \dots\dots (2.27) \end{aligned}$$

The second term in (2.27) can be evaluated essentially by the same means as (2.26) and the result is

$$a^4 \left\{ \frac{3}{8} - \frac{15\pi^2}{128} + \frac{1}{8} \pi^2 \log 2 - \frac{1}{16} \log^2 2 + \frac{3}{8} \sum_{n=1}^{\infty} \frac{1}{2^n n^3} \right\}. \quad \dots\dots (2.28)$$

To evaluate the first term in (2.27) notice that for small r

$$\int_0^{\infty} \frac{e^{-t}}{t} [E(t - r) - E(t + r)] dt = \frac{\pi^2}{4} + O(r \log r),$$

* In the original report the arrangement of calculations differed in one respect: the term involving $\{[r^2 - a^2] \log \{(r + a)/(r - a)\} - ra\}$ was excluded from the formula corresponding to (2.25) and was considered in connection with $\int \epsilon_3 \Lambda \epsilon_3 dr$.

and hence this first term becomes

$$\frac{3\pi^2}{32} a^4 E(a) + \frac{3}{8} a^4 \int_0^\infty \frac{e^{-r}}{r} \left\{ \int_r^\infty \frac{e^{-t}}{t} [E(t-r) - E(t+r)] dt - \frac{\pi^2}{4} \right\} dr + O(a^5). \dots (2.29)$$

The integral appearing in (2.29) after some rearrangement can be reduced to a form which can be evaluated by means of a series, and the expression (2.29) becomes

$$\frac{3\pi^2}{32} a^4 E(a) - \frac{3}{8} a^4 \sum_{n=0}^\infty \frac{1}{(2n+1)^3}. \dots (2.29')$$

§ 5. RESULTS

After substituting into (2.22) the expressions (2.23'), (2.25'), (2.26'), (2.28) and (2.29'), we ultimately obtain

$$q(\infty) = -\frac{3}{4} a^2 + \frac{a^3}{4} - \frac{3}{8} \left(\frac{\pi^2}{4} - 1 \right) a^4 \log a - 0.87095 + O(a^5 \log^k a), \dots (2.30)$$

while substituting this into (2.4) we have

$$\lambda = \frac{4}{3} - \frac{5}{9} a - 0.97827 a^2 \log a - 1.4002 a^2 + O(a^2 \log^k a). \dots (2.31)$$

PART III

CASE OF A LARGE BLACK CYLINDER

§ 1. TRANSFORMATION OF THE EQUATION

To reduce the equation (1) to a form suitable for the present case we should first of all perform the integration over the surfaces $r' = \text{const.}$ occurring in the right-hand side of that equation. It will be convenient to take for the three co-ordinates describing the position of the point $\bar{r}$, r' , z' and ρ where z' is measured along the axis of the cylinder, r' is the distance of the point r' from the axis of the cylinder, and ρ is the distance between the projections of the points r and r' on plane $z=0$. Then the equation (1) becomes

$$n(r) = \frac{2}{\pi} \int_a^\infty r' n(r') dr' \int_{|r-r'|}^{(r^2-a^2)^{1/2} + (r'^2-a^2)^{1/2}} \frac{d\rho}{\{\rho^2 - (r-r')^2\}^{1/2} \{(r+r')^2 - \rho^2\}^{1/2}} \int_0^\infty K_0(t) dt, \dots (3.1)$$

where $K_0(t)$ is the modified Bessel function of the second kind. If we expand $\{(r+r')^2 - \rho^2\}^{-1/2}$ in powers of $\{\rho^2 - (r-r')^2\}/4rr'$, and put

$$r = a + x; \quad r' = a + y; \quad r^{1/2} n(r) = C' q(x), \dots (3.2)$$

(in which C' is some constant) it can be re-written as

$$q(x) = \frac{1}{2} \int_0^\infty q(y) dy \sum_{n=0}^\infty \frac{|P_{2n}(0)|}{[4(a+x)(a+y)]^n} \times \{F_n(|x-y|) - \tilde{F}_n[|x-y|]; (2ax+x^2)^{1/2} + (2ay+y^2)^{1/2}\}, \dots (3.3)$$

in which $P_{2n}(s)$ are the Legendre polynomials and F_n and $\tilde{F}_n$ are defined by

$$\left. \begin{aligned} \tilde{F}_n(h; k) &= \frac{2}{\pi} \int_k^\infty [\rho^2 - h^2]^{n-1/2} \int_0^\infty K_0(t) dt d\rho; \quad (k \geq h \geq 0) \\ F_n(h) &= \tilde{F}_n(h, h). \end{aligned} \right\} \dots (3.4)$$

The functions $F_n(h)$ can be shown to be connected with the E -functions (defined in (5)) by the relationships

$$F_0(h) = E(h); \quad F_n(h) = (2n-1) \int_h^\infty t F_{n-1}(t) dt. \dots (3.5)$$

§ 2. NORMALIZATION OF THE SOLUTION AND THE ARRANGEMENT OF THE SUCCESSIVE APPROXIMATION

Before proceeding to solve equation (3.3) let us examine the behaviour of $q(x)$ for $x \gg a$, remembering that in our present case a in itself is very large ($a \gg 1$). Using the formulae (2) and (3) of the introduction, noticing that the general solution of the equation

$$\left(\frac{d^2}{dr^2} + \frac{1}{r} \frac{d}{dr}\right) n_{as}(r) = 0,$$

is $n_{as}(r) = A + B \log r$, and expressing here A and B in terms of the current at infinity and the linear extrapolation length λ we get at once

$$n(r) = [(r/a) n'(r)]|_{r=\infty} \{a \log r/a + \lambda + O(e^{-(r-a)})\}. \quad \dots (3.6)$$

Then if we write the constant C' in (3.2) in the form $C' = (1/C\sqrt{a}) [r n'(r)]|_{r=\infty}$ in which C is another constant to be determined later, the expression for $q(x)$ becomes

$$q(x) = C[a(1+x/a)^{1/2} \log(1+x/a) + \lambda(1+x/a)^{1/2} + O(e^{-x})]. \quad \dots (3.7)$$

In this expression the only quantities that are not already known apart from the common factor C are the constant λ and the terms of the order of e^{-x} . Both could be determined, for $a \gg 1$, by examining the variation of $q(x)$ in the region $x \ll a$. Now the kernel of the equation (3.3) for large $|x-y|$ is essentially of the order of $\exp(-|x-y|)$ so that if x is small compared with a , the contribution of the region of y either comparable with a or large compared with a , to the value of the right-hand side of (3.3) should be essentially of the order of e^{-a} . While the contribution of the region of $y \ll a$ to the values of $q(x)$ for $x \ll a$ will consist of terms of the order of unity, of the order of a^{-1} and so on.

This shows that, in so far as the determination of $q(x)$ for $x \ll a$ is concerned, we can replace (3.3) by the equation

$$\begin{aligned} q(x) = & \frac{1}{2} \int_0^\infty q(y) E(|x-y|) dy \\ & + \frac{1}{2} \int_0^\infty q(y) \left\{ \frac{|P_2(0)|}{4a^2} F_1(|x-y|) - \tilde{F}_0[|x-y|]; (2ax+x^2)^{1/2} + (2ay+y^2)^{1/2} \right\} dy \\ & + \frac{1}{2} \int_0^\infty q(y) \left\{ -(x+y) \frac{|P_2(0)|}{4a^3} F_1(|x-y|) \right\} dy + \dots \quad \dots (3.8) \end{aligned}$$

We solve this equation by the perturbation method, i.e. by putting

$$q(x) = q_0(x) + q_2(x) + q_3(x) + \dots \quad \dots (3.9)$$

in which $q_0(x)$, $q_2(x)$, $q_3(x)$ etc. satisfy the equations

$$q_0(x) = \frac{1}{2} \int_0^\infty q_0(y) E(|x-y|) dy \quad \dots (3.10.1)$$

$$\begin{aligned} q_2(x) = & \frac{1}{2} \int_0^\infty q_2(y) E(|x-y|) dy + \frac{1}{2} \int_0^\infty q_0(y) \left\{ \frac{|P_2(0)|}{4a^2} F_1(|x-y|) - \tilde{F}_0[|x-y|]; \right. \\ & \left. (2ax+x^2)^{1/2} + (2ay+y^2)^{1/2} \right\} dy \quad \dots (3.10.2) \end{aligned}$$

$$\begin{aligned} q_3(x) = & \frac{1}{2} \int_0^\infty q_3(y) E(|x-y|) dy - \frac{1}{2} \int_0^\infty q_0(y) (x+y) \frac{|P_2(0)|}{4a^3} F_1(|x-y|) dy \\ & - \frac{1}{2} \int_0^\infty q_2(y) \tilde{F}_0[|x-y|]; (2ax+x^2)^{1/2} + (2ay+y^2)^{1/2} dy, \quad \dots (3.10.3) \end{aligned}$$

and so on.

In the equations (3.8) and (3.10) we have extended the range of integration up to $y = \infty$, rather than integrating only over the range $y \ll a$, since this change in the

range of integration can affect the result for $x \ll a$ only by a quantity of the order of e^{-ax} , as in the original equation (3.3).

$q_0(x)$ is the solution of the Milne problem, and is known to be asymptotically linear in x . We have a normalizing condition, achieved by making $q_0'(\infty) = 1$. In so far as the other $q_n(x)$ is concerned, obviously if $q_n^*(x)$ is a possible solution of the equation for $q_n(x)$, so is $\{q_n^*(x) + Aq_0(x)\}$, where A is an arbitrary constant. We can, however, eliminate this arbitrariness by stipulating that the asymptotic expression for $q_n(x)$ for $x \gg 1$ should not contain a term proportional to x . Since the normalization of $q_0(x)$ was chosen in an arbitrary manner, the introduction of the above condition on $q_n(x)$ for $n > 0$ obviously will have no effect on the shape of $q(x) = \sum_{n=0}^{\infty} q_n(x)$.

The reason for combining the terms

$$(|P_2(0)|/4a^2) F_1(|x-y|) \quad \text{and} \quad -\tilde{F}_0[|x-y|; (2ax+x^2)^{1/2} + (2ay+y^2)^{1/2}]$$

in the expansion of the kernel of the equation (3.8) is as follows: With our restriction on the solutions of inhomogeneous equations of the type (3.10), the solution of the equation

$$q_{21}(x) = \frac{1}{2} \int_0^{\infty} q_{21}(y) E(|x-y|) dy + \frac{1}{2} \int_0^{\infty} q_0(y) \frac{|P_2(0)|}{4a^2} F_1(|x-y|) dy,$$

for $x \ll a$ is obviously of the order of a^{-2} . On the other hand, as is shown in Appendix B, the solution satisfying our restriction of the equation

$$q_{22}(x) = \frac{1}{2} \int_0^{\infty} q_{22}(y) E(|x-y|) dy - \frac{1}{2} \int_0^{\infty} q_0(y) \tilde{F}_0[|x-y|; (2ax+x^2)^{1/2} + (2ay+y^2)^{1/2}] dy \quad \dots (3.11)$$

is, for $x \gg a^{-1}$, also of the order of a^{-2} . Thus $q_2(x) = q_{21}(x) + q_{22}(x)$ is of the order of a^{-2} for $a^{-1} \ll x \ll a$, and this is just the range of values of x for which we need to know $q(x)$ in order to determine λ from (3.7).

It will be also shown in Appendix B that the appropriate solution of the equation

$$q_{32}(x) = \frac{1}{2} \int_0^{\infty} q_{32}(y) E(|x-y|) dy - \frac{1}{2} \int_0^{\infty} q_2(y) \tilde{F}_0[|x-y|; (2ax+x^2)^{1/2} + (2ay+y^2)^{1/2}] dy \quad \dots (3.12)$$

is, for $x \gg a^{-1}$, of the order of a^{-3} . So that $q_3(x)$ is for x in the range $a^{-1} \ll x \ll a$ of the order of a^{-3} and so on.

§ 3. EXPRESSION FOR λ IN TERMS OF ASYMPTOTIC PARTS OF $q_n(x)$

Considering the equations (3.10) for $n \neq 0$, one can easily show by induction that the free term of the equation for $q_n(x)$ is a polynomial in x of the order $(n-1)$ plus an exponentially decaying term $O(e^{-x})$; and hence $q_n(x)$ in itself should be equal to a polynomial in x of the order $(n+1)$ plus an exponentially decaying term $O(e^{-x})$.

Remembering also that $q_n(x)$ for $n \neq 0$ is assumed not to contain a term proportional to x , we can thus write

$$q_n(x) = \{x^2 Q_{n,2} + x^3 Q_{n,3} + \dots + x^{n+1} Q_{n,n+1}\} + \tilde{q}_n(x) \quad (n \geq 2) \quad \dots (3.13)$$

in which $\tilde{q}_n(x)$ is a bounded function and $Q_{n,m}$ are some constants; while $q_0(x)$ can be written as $q_0(x) = x + \tilde{q}_0(x)$ in which $\tilde{q}_0$ is also bounded. Substituting these into

(3.9) and noticing that for x tending to infinity $\tilde{q}_n(x)$ tend to constant values we get

$$q(x) = \sum_{n=0}^{\infty} q_n(\infty) + x + x^2 \sum_{n=2}^{\infty} Q_{n,2} + \dots + O(e^{-x})$$

while (3.7) can be re-written as

$$q(x) = C\lambda + xC \left(1 + \frac{\lambda}{2a}\right) + x^2 \frac{C\lambda}{8a^2} + \dots + O(e^{-x}).$$

Comparing the above two formulae we see at once that we should have $C(1 + \lambda/2a) = 1$; $C\lambda = \sum_{n=0}^{\infty} \tilde{q}_n(\infty)$ and hence eliminating C and solving with respect to λ we get

$$\lambda = \frac{\sum_{n=0}^{\infty} \tilde{q}_n(\infty)}{1 - \frac{1}{2a} \sum_{n=0}^{\infty} \tilde{q}_n(\infty)} = \sum_{m=0}^{\infty} \frac{1}{(2a)^m} \left\{ \sum_{n=0}^{\infty} \tilde{q}_n(\infty) \right\}^{m+1} \dots (3.14)$$

§ 4. SECOND AND THIRD APPROXIMATIONS: DERIVATION OF THE EXPRESSIONS FOR $\tilde{q}_2(\infty)$ AND $\tilde{q}_3(\infty)$

It is evident from (3.14) that in order to determine λ to the accuracy of $O(a^{-3})$ we should determine $\sum_{n=0}^{\infty} \tilde{q}_n(\infty)$ to the same accuracy. While since $q_n(x)$ is of the order of a^{-n} for $a^{-1} \ll x \ll a$, it follows from the definition of $\tilde{q}_n(x)$ that it is of $O(a^{-n})$ for all $x \gg a^{-1}$; and in particular $\tilde{q}_n(\infty)$ is of $O(a^{-n})$. Also $\tilde{q}_0(\infty)$ is already known and is equal to 0.7104... (Hopf 1934, p. 85). Thus, all that we need to determine is $\tilde{q}_2(\infty)$ and $\tilde{q}_3(\infty)$ to the accuracy of $O(a^{-3})$.

The polynomial parts of the free terms of the equations determining $q_2(x)$ and $q_3(x)$ can be easily worked out and are $\{x + \tilde{q}_0(\infty)\}/12a^2$ and $-\{6 + 5x[x + \tilde{q}_0(\infty)]\}/30a^3$ respectively. Then one can easily verify that the formulae (3.13) for $n=2$ and $n=3$ become

$$q_2(x) = \frac{-1}{24a^2} [x^3 + 3x^2 \tilde{q}_0(\infty)] + \tilde{q}_2(x), \quad q_3(x) = \frac{1}{24a^3} [x^4 + 2x^3 \tilde{q}_0(\infty)] + \tilde{q}_3(x). \dots (3.15)$$

Substituting these into (3.10), and expressing all the integrals of the form

$$\int_0^{\infty} y^m E_m(x+y) dy,$$

in terms of E_n functions we get for $\tilde{q}_2(x)$ and $\tilde{q}_3(x)$ the equations

$$\begin{aligned} \tilde{q}_2(x) &= \frac{1}{2} \int_0^{\infty} \tilde{q}_2(y) E(|x-y|) dy - \frac{1}{2} \int_0^{\infty} q_0(y) \tilde{F}_0 dy \\ &\quad + \frac{1}{16a^2} \left\{ [e^{-x} - 3E_3(x)] - \tilde{q}_0(\infty) [e^{-x} - 3E_1(x)] \right. \\ &\quad \left. + \int_0^{\infty} [q_0(y) - y - \tilde{q}_0(\infty)] [E_3(|x-y|) + |x-y|E_2(|x-y|)] dy \right\} \\ \text{and } \tilde{q}_3(x) &= \frac{1}{2} \int_0^{\infty} \tilde{q}_3(y) E(|x-y|) dy - \frac{1}{2} \int_0^{\infty} q_2(y) \tilde{F}_0 dy \\ &\quad + \frac{1}{16a^3} \{ [(3-x)e^{-x} - 15E_3(x)] - \tilde{q}_0(\infty) [(2-x)e^{-x} - 9E_3(x)] \\ &\quad - \int_0^{\infty} [q_0(y) - y - \tilde{q}_0(\infty)](x+y) [E_3(|x-y|) + |x-y|E_2(|x-y|)] dy \}, \end{aligned} \dots (3.16)$$

while using the formula (1.11) in Part I of this paper, i.e.

$$\tilde{q}_n(\infty) = 3 \int_0^\infty q_0(x) \{\text{the free term in the equation for } \tilde{q}_n(x)\} dx,$$

we finally get $\tilde{q}_2(\infty) = \{L_2 + \tilde{L}_2(a)\}/a^2$; $\tilde{q}_3(\infty) = \{L_3 + \tilde{L}_3(a)\}/a^3$, ... (3.17)
in which

$$\left. \begin{aligned} \tilde{L}_2(a) &= -\frac{3}{2} a^2 \int_0^\infty \int_0^\infty q_0(x) q_0(y) \tilde{F}_0[|x-y|; (2ax+x^2)^{1/2} + (2ay+y^2)^{1/2}] dx dy, \\ \tilde{L}_3(a) &= -\frac{3}{2} a^3 \int_0^\infty \int_0^\infty q_0(x) q_2(y) \tilde{F}_0[|x-y|; (2ax+x^2)^{1/2} + (2ay+y^2)^{1/2}] dx dy, \end{aligned} \right\} \text{..... (3.18)}$$

while the expressions for L_2 and L_3 are self-evident from the comparison of formulae (3.16), (3.17) and (3.18).

The expression for $\tilde{L}_3(a)$ depends upon $q_2(y)$. However, as it will be shown in Appendix B, of the two parts composing q_2 , viz. of q_{21} and q_{22} , the contribution of $q_{21}(y)$ to $\tilde{L}_3(a)$ will be of $O(a^{-4})$. Also if we substitute for $q_{22}(y)$ its expression from (3.11), only the free term of (3.11) will give a contribution of the order of a^{-3} while the contribution of the iterated term will be of $O(a^{-4})$. Thus in our present approximation we can replace the second formula (3.18) by

$$\tilde{L}_3(a) = \frac{3}{4} a^3 \int_0^\infty \int_0^\infty \int_0^\infty q_0(x) q_0(z) \tilde{F}_0[|x-y|; (2ax+x^2)^{1/2} + (2ay+y^2)^{1/2}] \tilde{F}_0[|y-z|; (2ay+y^2)^{1/2} + (2az+z^2)^{1/2}] dx dy dz + O(a^{-4}). \text{..... (3.18')}$$

§ 5. EVALUATION OF THE INTEGRALS APPEARING IN THE EXPRESSIONS FOR $\tilde{q}_2(x)$ AND $\tilde{q}_3(x)$

Consider first L_2 and L_3 . One can easily verify the identities*

$$\left. \begin{aligned} \frac{1}{2} \int_0^\infty q_0(y) E_2(|x-y|) \text{sign}(y-x) dy &= \frac{1}{3}, \\ \frac{1}{2} \int_0^\infty q_0(y) E_3(|x-y|) dy &= \frac{1}{3} \{x + \tilde{q}_0(\infty)\}, \\ \frac{1}{2} \int_0^\infty q_0(y) E_4(y) dy &= \frac{1}{5} + \frac{1}{3} \int_0^\infty [q_0(x) - x - \tilde{q}_0(\infty)] dx, \\ \frac{1}{2} \int_0^\infty q_0(y) E_5(y) dy &= \frac{1}{5} \tilde{q}_0(\infty) - \frac{1}{3} \int_0^\infty x [q_0(x) - x - \tilde{q}_0(\infty)] dx. \end{aligned} \right\} \text{..... (3.19)}$$

* These and other similar identities can be derived as follows, put:

$$S_n(x) = \frac{1}{2} \int_0^\infty q_0(y) E_n(|x-y|) \text{sign}(y-x)^{n-1} dy.$$

Then obviously

$$S'_{n+1}(x) = S_n(x) - (2n)^{-1} q_0(x) [1 - (-1)^n],$$

while for $x \rightarrow \infty$, from the asymptotic expression for $q_0(x)$ we get

$$S_n(x) \sim \{x + \tilde{q}_0(\infty)\}/n \quad \text{if } n \text{ is odd,} \quad S_n(x) \sim 1/(n+1) \quad \text{if } n \text{ is even.}$$

Combining these with (3.10) one can easily determine $S_n(x)$ by induction, and thus verify (3.19). Some of the identities (3.19) have been given by Hopf (1934, p. 30).

Using these identities and the recurrence formula for the E_n functions, one can eliminate all the double integrals in the expressions for L_2 and L_3 , as well as all the integrals involving E_n functions, obtaining

$$\left. \begin{aligned} L_2 &= \frac{3}{40} \tilde{q}_0(\infty) + \frac{1}{8} \tilde{q}_0(\infty) \int_0^\infty [q_0(x) - x - \tilde{q}_0(\infty)] dx - \frac{1}{8} \int_0^\infty x [q_0(x) - x - \tilde{q}_0(\infty)] dx \\ L_3 &= \frac{3}{40} [\tilde{q}_0(\infty)]^2 - \frac{1}{4} \tilde{q}_0(\infty) \int_0^\infty x [q_0(x) - x - \tilde{q}_0(\infty)] dx. \end{aligned} \right\} \dots\dots(3.20)$$

The integrals appearing in (3.20) have been already considered by Mark (1944) who has found that

$$\left. \begin{aligned} \int_0^\infty [q_0(x) - x - \tilde{q}_0(\infty)] dx &= -\left\{ \frac{3}{10} - \frac{1}{2} [\tilde{q}_0(\infty)]^2 \right\}, \\ \text{and} \quad \int_0^\infty x [q_0(x) - x - \tilde{q}_0(\infty)] dx &= -0.025993. \end{aligned} \right\} \dots\dots(3.21)$$

Turn now to the integrals $\tilde{L}_2(a)$ and $\tilde{L}_3(a)$. These are quite similar to the integrals (1.18) occurring in Part I of this paper. Following the same method as there, and noticing that

$$\tilde{F}_0((a^2 + s^2)^{1/2} - (a^2 + t^2)^{1/2}; s+t) = \frac{2}{\pi} \int_{s+t}^\infty K_0(z) \log \frac{z}{s+t} dz + O(a^{-2}),$$

we obtain after a slight rearrangement

$$\tilde{L}_2(a) = -\frac{1}{\pi} \int_0^\infty \int_0^\infty st \left[1 + \frac{s^2}{2a} (\log 2a + 2c_1) - \frac{s^2 \log s}{a} + O\left(\frac{\log^2 a}{a^2}\right) \right] G(s+t) ds dt \dots\dots(3.22)$$

and

$$\tilde{L}_3(a) = \frac{1}{\pi^2} \int_0^\infty \int_0^\infty \int_0^\infty ds_1 ds_2 ds_3 G(s_1 + s_2) G(s_2 + s_3) + O\left(\frac{\log a}{a}\right) \dots\dots(3.22')$$

in which

$$G(s) = \int_s^\infty K_0(z) \log(z/s) ds. \dots\dots(3.22'')$$

An exact expression can be obtained for the integrals occurring in $\tilde{L}_2(a)$ and $\tilde{L}_3(a)$ can be expressed in terms of rapidly converging series as follows:

$$\tilde{L}_2(a) = -\frac{3}{64} - \frac{5 \log a}{64 a} + \frac{1}{a} \left\{ \frac{137}{384} - \frac{5}{64} (2c_1 + 2\gamma + \log 8) \right\} + O\left(\frac{\log^2 a}{a^2}\right) \dots(3.23)$$

in which c_1 and γ have the same meaning as in Part I of this paper and

$$\begin{aligned} L_3(a) &= \frac{15}{16\pi^2} \sum_{n=0}^\infty \frac{1}{(2n+1)^3} - \frac{5}{16\pi^2} \sum_{n=1}^\infty \frac{1}{2^n n^3} + \frac{5 \log^2 2}{96 \pi^2} - \frac{5 \log 2}{192} \\ &\quad - \frac{347}{864 \pi^2} - \frac{19}{768} + O\left(\frac{\log a}{a}\right). \dots\dots(3.23') \end{aligned}$$

§ 6. RESULTS

Carrying out the summation in the series (3.23'), using the known values of γ , c_1 , $\tilde{q}_0(\infty)$ and (3.21), substituting (3.23) and (3.20) into (3.17) and then the latter into (3.14) we ultimately obtain

$$\lambda = 0.7104 \dots + 0.2524 \dots a^{-1} + 0.0949 a^{-2} - \frac{5}{64} a^{-3} \log a - 0.01634 a^{-3} + O\left(\frac{\log^2 a}{a^4}\right) \dots\dots(3.24)$$

PART IV

SMALL BLACK CYLINDER AND BLACK SPHERE AND BLACK CYLINDER OF INTERMEDIATE SIZE

§ 1. CASE OF A SMALL BLACK CYLINDER

The solution of the problem for the case of a small black cylinder has been given by Kushneriuk (1951) and we shall limit ourselves here to a short abstract of that work, to which the reader is referred for all the details.

The equation governing $n(r)$ is the same as the equation (3.1) which, on putting

$$K(r, r'; a) = \frac{2}{\pi} \int_{|r-r'|}^{(r^2-a^2)^{1/2} + (r'^2-a^2)^{1/2}} \frac{d\rho}{\{\rho^2 - (r-r')^2\}^{1/2} \{(r+r')^2 - \rho^2\}^{1/2}} \int_0^\infty K_0(t) dt \quad \dots\dots(4.1)$$

$$\text{can be re-written as } n(r) = \int_a^\infty r' n(r') K(r, r'; a) dr' \quad (r \geq a). \quad \dots\dots(4.2)$$

Following the same method as is adopted in Part II of the present paper, the definition of $n(r)$ is extended to $0 \leq r < a$ by putting

$$n(r) = \int_a^\infty r' n(r') K(r, r'; 0) dr' \quad (r < a) \quad \dots\dots(4.2')$$

and the solution is sought in the form

$$n(r) = n_0(r) + n_1(r) + \dots \quad \dots\dots(4.3)$$

in which the successive $n_m(r)$ satisfy the equations

$$\left. \begin{aligned} n_0(r) &= \int_0^\infty r' n_0(r') K(r, r'; 0) dr' \\ n_m(r) &= \int_0^\infty r' n_m(r') K(r, r'; 0) dr' + f_m(r) \quad (m \geq 1) \end{aligned} \right\} \quad \dots\dots(4.4)$$

in which

$$f_m(r) = S(r-a) \int_a^\infty r' n_{m-1}(r') [K(r, r'; a) - K(r, r'; 0)] dr' - \int_0^a r' n_{m-1}(r') K(r, r'; 0) dr' \quad \dots\dots(4.5)$$

and $S(r-a) = 1$ for $r > a$ and zero for $r < a$; $n(r)$ is normalized so that

$$\lambda[(r/a)n'(r)]_{r=\infty} = 1. \quad \dots\dots(4.6)$$

Consistent with this normalization one can take $n_0(r) \equiv 1$ and normalize various $n_m(r)$ for $m \geq 1$ so that, for $r \rightarrow \infty$, $n_m(r)$ behaves as

$$n_m(r) = B_m(a) \log r/a + O(e^{-r}). \quad \dots\dots(4.7)$$

Then, as one can easily see, λ will be given by

$$\lambda = a \left/ \sum_{m=1}^{\infty} B_m(a) \right. \quad \dots\dots(4.8)$$

To solve the equations (4.4) for $m \geq 1$, we can use the following formula:

$$n_m(r) = \iiint p(R) f_m(r_0) dx_0 dy_0 dz_0 + f_m(r) \quad \dots\dots(4.9)$$

(this is analogous to (2.12) of the second section) in which R is the distance between the points (x, y, z) and (x_0, y_0, z_0) and $p(R)$ is the neutron density due to a point source of unit strength in an infinite isotropically scattering medium, at the distance

R from the point source. Substituting the explicit expression for $p(R)$, choosing the additive arbitrary constant entering that expression so as to satisfy (4.7), one can re-write (4.9) as

$$n_m(r) = B_m(a) \log r/a + f_m(a) - 3 \int_r^\infty \{\log(r'/r)\} r' f_m(r') dr' + \frac{1}{2\pi} \int_1^\infty g(y) dy \int_0^\infty r' f_m(r') dr' \int_0^{2\pi} K_0\{y(r^2 + r'^2 - 2rr' \cos \theta)^{1/2}\} d\theta \dots (4.10)$$

$$\text{in which} \quad B_m(a) = -3 \int_0^\infty r' f_m(r') dr' \dots (4.11)$$

$$\text{and} \quad g(y) = \left\{ 1 + \frac{1}{y} \log \frac{y-1}{y+1} + \frac{1}{4y^2} \left(\pi^2 + \log^2 \frac{y-1}{y+1} \right) \right\}^{-1} \dots (4.12)$$

In applying these formulae, it is necessary to determine beforehand the order of magnitude of various terms, so as to avoid carrying out lengthy calculations of quantities which would be subsequently found to be negligible. The main result in this direction is as follows. If, for some m , $f_m(r)$ satisfies the inequalities $|f_m(r)| < A_m e^{-r}/r$ for $r > a$, $|f_m(r)| < A_m$ for $r < a$, then $f_{m+1}(r)$ satisfies the same inequalities, with $A_{m+1} < C A_m a \log a^{-1}$, in which C is some constant independent of m . Using this result one can show, for instance, that if we wish to determine λ to an accuracy of $O(a)$ i.e. neglecting terms of $O(a^2 \log^2 a^{-1})$, it is sufficient to evaluate $B_1(a)$ and $B_2(a)$. Working out of these two coefficients gave $B_1(a) = \frac{3}{4}a + O(a^3)$, $B_2(a) = (3/\pi^2) - (9/16) a^2 \log a + 0.1217 a^2 + O(a^3 \log a)$ and hence

$$\lambda = 4/3 + (1 - 16/3\pi^2) a \log a - 0.2164a + O(a^2 \log^2 a).$$

§ 2. BLACK SPHERE AND BLACK CYLINDER OF INTERMEDIATE SIZE

The preceding Parts of this paper dealt only with the determination of λ for the cases of small and large values of the radius, rather than with the case of the radius comparable with unity. In this latter case the exact determination of λ is impossible, and one has to resort to approximate methods, to which reference has been made in the introduction. However, supplementing the results of the application of the approximate methods with the values of λ for small a and for large a from Parts I to IV and from Kushneriuk's paper, one can judge fairly accurately what the exact values of λ are for intermediate values of a . This is illustrated in Figures 1 and 2. Figure 1 refers to the case of a black sphere. The curves I and II correspond to the expressions for λ for small and large a derived in Parts I and II of the present paper. The curves III(a) to III(d) represent the results of Mark's calculation of λ by the spherical harmonics method using P_3 to P_7 approximations, the application of this latter method to the case of a black sphere has already been described by Marshak*. From the comparison of these curves, the curve IV was drawn, joining smoothly curves I and II for small and large a , and having the same shape as the curves III for intermediate values of a ; there is

* See Marshak (1947 b). Actually the method that had been adopted by Mark differed slightly from that described by Marshak. Namely, instead of the boundary conditions used by Marshak, Mark used the alternative boundary conditions, outlined in the footnote on p. 444 of Marshak's paper. In determining even order spherical harmonics approximation, Mark was allowing discontinuities in the even order moment at the boundary, but was stipulating that the discontinuity should be proportional to the infinite part of the derivative of the true value of the corresponding moment.

very little doubt that the curve IV represents the dependence of λ upon a quite accurately.

Figure 2 refers to the case of a black cylinder. Here the curves I and II correspond to the expressions for λ derived in Part III, and in Kushneriuk's paper, while the curve III represents the result of calculating λ by the spherical harmonics method in P_3 approximation. Though higher order spherical harmonic approximations have not been calculated for the case of a black cylinder,

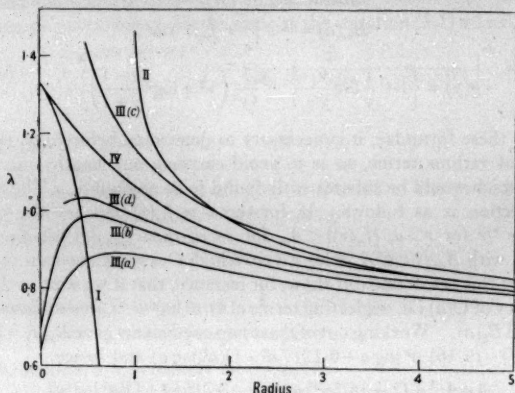


Figure 1. Extrapolation length λ , in terms of radius of the sphere: I, small black sphere; II, large black sphere; III (a) (b) (c) (d), spherical harmonics (P_3 , P_5 , P_6 and P_7 approximations respectively); IV, probable shape of dependence for a sphere of finite radius. Units in terms of mean free path.

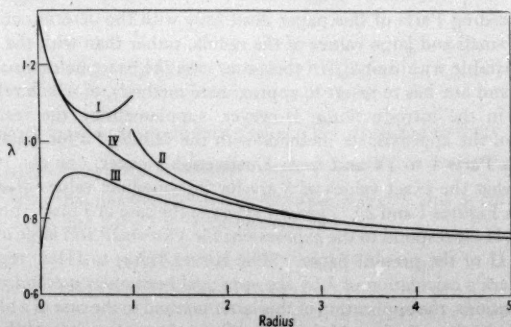


Figure 2. Extrapolation length λ , in terms of the radius of the cylinder: I, small black cylinder; II, large black cylinder; III, spherical harmonics (P_3 approximation); IV, probable shape of dependence for a cylinder of finite radius. Units in terms of mean free path.

the comparison with the spherical case indicates that shape of the $\lambda(a)$ curve for a comparable with unity should be given quite accurately in the P_3 approximation. The comparison of the curves I, II and III then leads one to expect that the correct dependence of λ on a for the case of a black cylinder should be as indicated by the curve IV of Figure 2.

APPENDIX A

Proof of the Inequality (1.16)

Consider simultaneously with (1.5) the equation

$$h(x) = \frac{1}{2} \int_0^\infty h(y) E(|x-y|) dy + E(x)$$

imposing upon $h(x)$ the condition $h'(\infty) = 0$, similar to (1.6). Both $h(x)$ and $q_n(x)$ are, in Hopf's terminology, N -solutions, and by a lemma proved by Hopf

$$q_n(0) - f_n(0) = \frac{1}{2} \int_0^\infty q_n(x) E(x) dx = \frac{1}{2} \int_0^\infty f_n(x) h(x) dx. \quad \dots (A1)$$

On the other hand $h(x)$ is obviously of the form $h(x) = E(x) +$ a bounded function. Then proceeding as in the derivation of (1.13) and (1.15) we can easily show that the right-hand side of (A1) is of the order of $(a^{-n-1} \log a)$. This establishes (1.16) for $x=0$. To prove this for $x \neq 0$ from (1.5) we obtain

$$q_n(x) - f_n(x) = [q_n(0) - f_n(0)] + \frac{1}{2} \int_0^\infty q_n(y) [E(|x-y|) - E(y)] dy.$$

On the grounds of the estimates obtained previously, this means

$$q_n(x) - f_n(x) = O(a^{-n-1} \log a) + a^{-n} O \left[\int_0^\infty \{ |E(|x-y|) - E(y)| \} dy \right]$$

and (1.16) then follows at once.

APPENDIX B

The Order of Magnitude of $q_{22}(x)$ and $q_{32}(x)$

Notice that

$$\tilde{F}_0[|x-y|; (2ax+x^2)^{1/2} + (2ay+y^2)^{1/2}] < \tilde{F}_0\{(2ax+x^2)^{1/2} + (2ay+y^2)^{1/2}; \\ (2ax+x^2)^{1/2} + (2ay+y^2)^{1/2}\} = E\{(2ax+x^2)^{1/2} + (2ay+y^2)^{1/2}\}.$$

Then the free term of the equation (3.11) is of the same order of magnitude, for each particular x , as $f_1(x)$ in Part I. Also, with the free term decreasing exponentially as x tends to ∞ , the stipulation that $q_{22}(x)$ should not contain a term proportional to x for large x is equivalent to the stipulation that $q_{22}(x)$ is a bounded solution of (3.11). Then the order of magnitude of $q_{22}(x)$ and of the iterated term in (3.11) should be also identical with the order of magnitudes of $q_1(x)$ and of $\frac{1}{2} \int_0^\infty q_1(y) E(|x-y|) dy$ of Part I respectively. From the analysis given in Part I we see then that $q_{22}(x) = O(a^{-2} \log a)$ for $x \gg a^{-1}$ and that the iterated term in (3.11) is of the order of $a^{-2} \log a$ for any value of x . This proves the estimate of $q_{22}(x)$ quoted in connection with (3.11).

To prove the estimate quoted for $q_{32}(x)$ put $q_{32}(x) = q_{321}(x) + q_{322}(x)$ in which $q_{321}(x)$ is defined by the equation (3.12) with $q_2(y)$ in the integrand of the free term replaced by $\{q_{21}(y) + \text{the iterated term of (3.11)}\}$ and $q_{322}(x)$ is defined by the same equation with $q_2(y)$ replaced by the free term of (3.11). Now it is obvious that the free term of the equation for $q_{321}(x)$ is of the order of $a^{-2} \log a$ as compared with the free term of (3.11) and consequently $q_{321}(x) = O(a^{-2} \log a)$ $q_{22}(x) = O(a^{-4} \log^2 a)$

except for x comparable with a^{-1} , while the free term of the equation for $q_{322}(x)$ is of the same order as

$$\int_0^\infty \int_0^\infty E\{(2ax + x^2)^{1/2} + (2ay + y^2)^{1/2}\} E\{(2ay + y^2)^{1/2} + (2az + z^2)^{1/2}\} dy dz$$

which for any particular x is of the order of a^{-1} as compared with the free term of (3.11). Then $q_{322}(x) = O(a^{-1}q_{22}(x))$ and this proves the estimate of $q_{32}(x)$ quoted in connection with (3.12).

ACKNOWLEDGMENTS

The author wishes to thank Sir John Cockcroft for the permission to publish this work, and Dr. J. H. Tait for his valuable help in editing the present paper.

REFERENCES

- BOTHE, W., 1942, *Z. Phys.*, **119**, 493.
 DAVISON, B., 1944, 1945, *Canadian Declassified Reports* (of the Montreal, later of Chalk River, Ontario, Laboratories of N.R.C.), MT. 88, MT. 93, and MT. 135.
 DAVISON, B., and KUSHNERIUK, S., 1946, *Canadian Declassified Reports*, MT. 214.
 HOPF, E., 1934, *Cambridge Tracts in Mathematics and Mathematical Physics*, **31**.
 KUSHNERIUK, S., 1951, *Proc. of 2nd Canadian Math. Congress* (1949), in the press.
 MARK, C., 1944, *Canadian Declassified Reports*, MT. 50.
 MARSHAK, R. E., 1947 a, *Phys. Rev.*, **71**, 688; 1947 b, *Ibid.*, **71**, 443.
 PEIERLS, R. E., 1939, *Proc. Camb. Phil. Soc.*, **35**, 610.
 SEIDEL, W., DAVISON, B., and KUSHNERIUK, S., 1946, *Canadian Declassified Reports*, MT. 207.
 TITCHMARSH, E. C., 1937, *Introduction to the Theory of Fourier Integrals* (Oxford: University Press).

The Excitation Function for the Production of ${}^7\text{Be}$ by the Bombardment of ${}^{12}\text{C}$ by Protons

BY J. M. DICKSON AND T. C. RANDLE

Atomic Energy Research Establishment, Harwell, Didcot, Berks.

Communicated by D. W. Fry; MS. received 9th February 1951, and in amended form 15th May 1951

ABSTRACT. The excitation function for the production of ${}^7\text{Be}$ from ${}^{12}\text{C}$ has been determined by an activation method, using the internal proton beam of the 110-inch Harwell cyclotron. The threshold energy has been found to be 32 mev. and the cross section at 156 mev. is $11.0 \pm 1.3 \times 10^{-27} \text{ cm}^2$.

§1. INTRODUCTION

IN a previous paper (Dickson and Randle 1950) evidence was presented for the production of ${}^7\text{Be}$ by proton bombardment of ${}^{12}\text{C}$, and a preliminary value of the cross section was given. Further experiments have been made by bombarding carbon targets at various radii in the internal beam of the Harwell cyclotron, in order to determine the excitation function up to 156 mev.

Although it is convenient to refer to the process as the reaction ${}^{12}\text{C}(p, 3p3n){}^7\text{Be}$, the protons and neutrons are not necessarily ejected as six separate particles. It will in fact be shown that they are certainly not ejected in this way at the lower proton energies.

§ 2. EXPERIMENTAL METHOD

The carbon targets were semi-circular discs $\frac{1}{8}$ in. thick by $\frac{3}{4}$ in. radius, and were known to contain very little impurity. For each irradiation one of these discs was mounted with its diametral edge vertical and facing towards the centre of the cyclotron. In addition to ^7Be , ^{11}C was produced in the target by the reaction $^{12}\text{C}(\text{p}, \text{pn})^{11}\text{C}$. Since the cross section for this reaction has been published, from the threshold (18.5 mev.) to 350 mev., by Aamodt, Peterson and Phillips (1949), the ^{11}C activity could be used to monitor each bombardment.

After irradiation the target was enclosed in an aluminium sheath, whose thickness was twice the range of positrons from ^{11}C , and the activity was measured by an end-window Geiger counter. The radiation detected consisted of annihilation radiation from the positrons of ^{11}C (half-life 20 minutes) and nuclear γ -radiation from ^7Be (half-life 53 days). Activities with half-lives of a few hours were also detected, but the counting rates due to these were low. From the decay-plot of γ -activity against time the counting rates $N(^{11}\text{C})$ and $N(^7\text{Be})$ due to ^{11}C and ^7Be at the end of the irradiation were calculated. These are related to the disintegration rates $D(^{11}\text{C})$ and $D(^7\text{Be})$ as follows: $N(^{11}\text{C}) = 2D(^{11}\text{C})E(^{11}\text{C})$, $N(^7\text{Be}) = RD(^7\text{Be})E(^7\text{Be})$ where $E(^{11}\text{C})$ and $E(^7\text{Be})$ are the efficiencies of the Geiger counter for the two γ -rays and R is the branching ratio of the ^7Be decay.

Since the periods of irradiation were comparable with the half-life of ^{11}C a correction factor $\{1 - \exp \lambda(^{11}\text{C})t\} / \lambda(^7\text{Be})t$ was applied to the observed ratio of the two activities, where $\lambda(^{11}\text{C})$ and $\lambda(^7\text{Be})$ are the disintegration constants of ^{11}C and ^7Be and t is the duration of the irradiation. The cross section $\sigma(^7\text{Be})$ for the production of ^7Be was evaluated relative to the cross section $\sigma(^{11}\text{C})$ for the production of ^{11}C by the formula

$$\sigma(^7\text{Be}) = \sigma(^{11}\text{C}) \frac{1 - \exp \lambda(^{11}\text{C})t}{\lambda(^7\text{Be})t} \frac{N(^7\text{Be})}{N(^{11}\text{C})} \frac{E(^{11}\text{C})^2}{E(^7\text{Be})R}.$$

The value assumed for the branching ratio R was 0.123 and the counter efficiency ratio, $E(^{11}\text{C})/E(^7\text{Be})$ was 1.04.

Effective Proton Energy

The thickness in mev. of the $\frac{1}{8}$ in. thick carbon targets varied from 2.3 mev. for 175 mev. protons to 9 mev. for 35 mev. protons. The beam, however, traversed the target several times (Cassels, Dickson and Howlett 1951), causing an even wider spread in bombarding energy. The effective thickness of the targets was 18.5 mev. at 175 mev. and 13.5 mev. at 35 mev. The cross sections were evaluated for the effective proton energy, i.e. the bombarding proton energy minus the effective target thickness. A few $\frac{1}{16}$ in. thick targets were irradiated in such a way that the beam was prevented by a shutter arrangement from traversing the target more than once; all those protons which had been scattered by more than a very small angle during the first traversal of the target were absorbed by the shutter. These irradiations, at energies from 35 to 50 mev., were used to determine the threshold energy.

Half-life of ^{11}C

The ^{11}C could not be counted until 4 to 5 hours after irradiation on account of its initial high intensity, but the counting rate after five hours could be estimated to an accuracy closer than 1%. Several short irradiations of carbon and polythene, producing relatively weak sources of ^{11}C with negligible quantities of any other activities, were used to measure the half-life of ^{11}C . The average

value of six runs, each extending over at least six half-lives, was 20.0 ± 0.1 minutes. Values of 20.0 , 20.35 ± 0.08 , 20.5 ± 0.6 minutes are given in the literature by Siegbahn and Bohr (1944), Smith and Cowie (1941) and Solomon (1941), but it was decided to use the value 20.0 minutes to calculate the initial ^{11}C activity from the counting rate after 5 hours. The error introduced in each measurement of the ^7Be cross section, by an error in the half-life of ^{11}C , will not affect the shape of the excitation function but only the absolute values of the cross section.

Half-life of ^7Be

Measurement of the half-life of ^7Be gave the value 53 ± 2 days; the generally accepted value of 52.93 ± 0.22 days, measured by Segrè and Wiegand (1949), was used.

Branching Ratio

^7Be decays by K-capture either to ^7Li in the ground state or to ^7Li in the 480 kev. excited state with the subsequent emission of a γ -ray. The branching ratio R for this process has been measured by Turner (1949) and by Williamson and Richards (1949). Their results were $0.118 \pm 10\%$ and 0.107 ± 0.02 , respectively. Turner's work was less liable to systematic error since it involved comparing counting rates and computing a counter efficiency ratio for two γ -rays (0.51 and 0.48 mev.), while the measurement by Williamson and Richards involved two absolute calibrations of counters. Turner, however, used the value of 20.5 ± 0.6 minutes for the half-life of ^{11}C . He also had to find the ratio of the efficiencies of his counter for annihilation radiation and 0.48 mev. γ -rays. When the latest values for the mass absorption coefficients (Snyder and Powell 1949) are inserted in Turner's formula for the efficiency ratio, together with the value of 20.0 minutes for ^{11}C half-life, the value of the branching ratio becomes $0.123 \pm 5\%$. This value has been used for evaluating our results.

Counter Calibration

The counter efficiency for 0.51 mev. γ -rays was measured by counting the annihilation radiation from a thin ^{11}C source and later counting the positrons in a defined solid angle β -counter. The value found was 6.0×10^{-4} . The efficiency for 0.411 mev. γ -rays was measured by counting the γ -rays from a standardized ^{198}Au source, and found to be 5.2×10^{-4} . By interpolating these results the counter efficiency ratio, $E(^{11}\text{C})/E(^7\text{Be})$ was calculated to be $1.04 \pm 5\%$.

§ 3. RESULTS

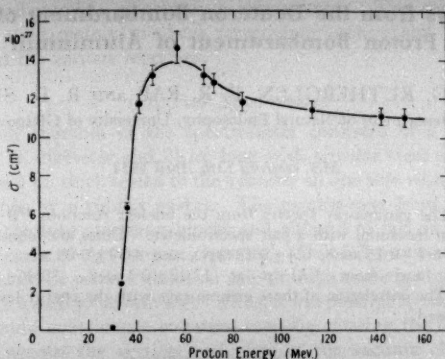
Twenty-five carbon targets were bombarded at effective energies between 35 mev. and 156 mev. to determine the excitation function. Six carbon targets were bombarded for very short periods to determine the half-life of ^{11}C .

The yields of ^{11}C and ^7Be in the 25 carbon targets per min. of irradiation were about 8×10^7 and 500 counts per min. respectively at 156 mev. effective proton energy, falling to 2.5×10^7 and 100 counts per min. at 50 mev.

The excitation function is plotted in the Figure. The yield of ^7Be rises sharply above 32 mev. The cross section is very small (less than $0.1 \times 10^{-27} \text{ cm}^2$) at 30 mev., reaches a maximum of $13.8 \times 10^{-27} \text{ cm}^2$ at about 55 mev. and falls slowly to $11 \times 10^{-27} \text{ cm}^2$ at 156 mev.

The threshold energies for the reaction, calculated for all combinations of (3p3n), range from 24.4 to 59.0 mev. (see Table). It is evident that the (3p3n) are

not produced as six separate particles and that the first three groupings in the Table are the only possible products of the reaction near the threshold energy.



Excitation function for the production of ${}^7\text{Be}$ by the bombardment of ${}^{13}\text{C}$ by protons. The deviations shown in the figure are the compounded sum of errors due to counting statistics and errors quoted for the ${}^{13}\text{C}(p, pn){}^{11}\text{C}$ cross section. In addition there is an uncertainty of 8% which can only affect the curve as a whole, without changing its shape. This arises from uncertainties in (1) ${}^7\text{Be}$ branching ratio, (2) ${}^{13}\text{C}$ half life and (3) the γ -ray efficiency ratio of the Geiger counter. When combining this error with those shown in the diagram, the normal square law should be used.

Products of reaction	Q (mev.)	Threshold (mev.)
${}^7\text{Be} + {}^4\text{Li}$	-22.6	24.4
${}^7\text{Be} + {}^4\text{He} + {}^3\text{H}$	-24.1	26.1
${}^7\text{Be} + {}^4\text{He} + p + n$	-26.3	28.5
${}^7\text{Be} + {}^3\text{He} + {}^3\text{H}$	-38.5	41.7
${}^7\text{Be} + {}^3\text{H} + 2p + n$	-46.2	50.0
${}^7\text{Be} + {}^3\text{H} + p + 2n$	-46.9	50.8
${}^7\text{Be} + {}^3\text{H} + {}^3\text{H} + p$	-44.0	47.6
${}^7\text{Be} + 3{}^3\text{H}$	-48.0	52.0
${}^7\text{Be} + 3p + 3n$	-54.6	59.0

ACKNOWLEDGMENTS

The authors are indebted to Dr. T. G. Pickavance for suggesting this experiment and for his helpful advice in technical and theoretical problems associated with the work, and wish to thank the team operating the cyclotron for their co-operation during these experiments.

This paper is published by permission of the Director, Atomic Energy Research Establishment, Harwell.

REFERENCES

- AAMODT, L., PETERSON, V., and PHILLIPS, R., 1949, *University of California Radiation Laboratory Report*, No. 526.
 CASSELS, J. M., DICKSON, J. M., and HOWLETT, J., 1951, *Proc. Phys. Soc. B*, **64**, 590.
 DICKSON, J. M., and RANDLE, T. C., 1950, *Nature, Lond.*, **166**, 235.
 SEGRÉ, E., and WIEGAND, C. E., 1949, *Phys. Rev.*, **75**, 39.
 SIEGBAHN, K., and BOHR, E., 1944, *Ark. Mat. Astr. Fys.*, **30B**, No. 3.
 SMITH, J. H. C., and COWIE, D. B., 1941, *J. Appl. Phys.*, **12**, 78.
 SNYDER, W. S., and POWELL, J. L., 1949, *Atomic Energy Commission (U.S.A.) Declassified Report*, No. 2739.
 SOLOMON, A. K., 1941, *Phys. Rev.*, **60**, 279.
 TURNER, C. M., 1949, *Atomic Energy Commission (U.S.A.) Unclassified Report*, No. 432.
 WILLIAMSON, R. M., and RICHARDS, H. T., 1949, *Phys. Rev.*, **76**, 614.

Gamma-Rays from the Deuteron Bombardment of Boron and the Proton Bombardment of Aluminium

By J. G. RUTHERGLEN, E. R. RAE AND R. D. SMITH

Department of Natural Philosophy, University of Glasgow

MS. received 13th April 1951

ABSTRACT. The gamma-ray spectra from the nuclear reactions $^{10}\text{B} + \text{d}$, $^{11}\text{B} + \text{d}$, and $^{27}\text{Al} + \text{p}$ have been measured with a pair spectrometer. Lines are found from $^{10}\text{B} + \text{d}$ at 8.88 ± 0.06 mev., 6.7 ± 0.15 mev., 6.4 ± 0.15 mev., and 4.38 ± 0.05 mev.; from $^{11}\text{B} + \text{d}$ at 4.44 ± 0.05 mev.; and from $^{27}\text{Al} + \text{p}$ at 12.12 ± 0.1 mev., 10.46 ± 0.07 mev., and 7.62 ± 0.1 mev. The correlation of these gamma-rays with the energy levels of the nuclei involved is discussed.

§ 1. INTRODUCTION

THE study of the energy and intensity of the high energy gamma-rays emitted in nuclear reactions has received comparatively little attention because of the lack of suitable techniques, particularly in cases where the gamma-ray spectrum is complex. However, the development of a pair spectrometer by Walker and McDaniel (1948) has made it possible to measure the spectra of high-energy gamma-rays with greatly improved resolution and efficiency.

We have, therefore, applied this technique to the measurement of the gamma-ray spectra from a number of nuclear reactions for which our particle accelerator, which supplies a comparatively large beam current at potentials up to 800 kv., is particularly suitable. The results of an investigation of the proton capture radiation from ^{19}F have already been published (Rae *et al.* 1950). Measurements on the radiations produced when ^{10}B and ^{11}B are bombarded by deuterons, and ^{27}Al by protons, are presented in this paper, together with a description of the experimental technique.

§ 2. APPARATUS

(i) Generator

A cascade generator was used to accelerate protons or deuterons to a maximum energy of 800 kev. A magnetically resolved beam current of up to $150 \mu\text{a.}$ was available at the target. A complete description of this generator and its radio-frequency ion source will be published shortly.

(ii) Target Arrangements

The general arrangement of the target assembly and pair spectrometer is shown in Figure 1. The resolved beam from the accelerator tube emerged from the resolving chamber down the axis of a glass tube inclined at 30° to the vertical. A shallow water-cooled brass cup was sealed by a demountable rubber gasket joint to the end of this tube. Targets were normally prepared on thin brass or copper discs, which were clamped to the inside of the cup. The cup was insulated from ground and was connected to the input of a current integrator of conventional design.

A Geiger counter with thick aluminium walls was mounted at a fixed distance from the target and was used to monitor the gamma-ray intensity. All runs were made for a fixed number of counts in this counter. The current integrator readings were used mainly to check target deterioration and to estimate the relative yield of the various reactions.

(iii) Pair Spectrometer

The vacuum chamber of the spectrometer consisted of a circular copper cylinder 12 in. in diameter and $2\frac{1}{2}$ in. long with circular steel end plates 14 in. in diameter and $\frac{1}{2}$ in. thick sealed to the cylinder on one side with a soldered joint and on the other by a rubber gasket. The gamma-rays from the target were collimated by the lead shielding blocks and allowed to fall on a thin lead foil placed at the centre of the vacuum chamber. This foil was mounted on a light frame which could be rotated about an axis through one edge by means of a rod passing through a rotary vacuum seal. Thus, it was possible to take measurements of the background coincidence counting rates by rotating the foil through 90° , so that it lay against the vertical end plate of the vacuum chamber. These

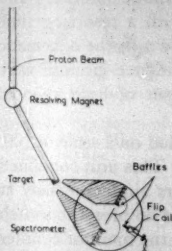


Figure 1. General arrangement.

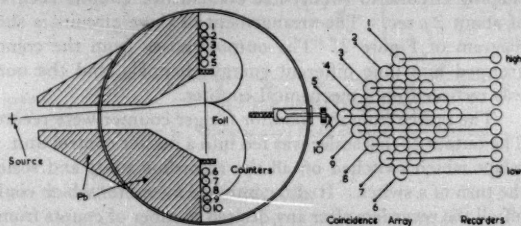


Figure 2. Block schematic diagram of spectrometer and recording circuits.

background rates were negligible when measurements were made on proton reactions, but were often serious in deuteron reactions because of the difficulty of providing adequate screening of the counters from the gamma-rays produced by the accompanying neutrons.

The chamber was placed between the 12 in. diameter poles of an electromagnet of conventional design which provided a field of up to 7,000 gauss. This field was sufficient to measure gamma-ray energies up to 30 mev. The field was measured by means of a flip coil and fluxmeter. The relative accuracy of this measurement was estimated to be within approximately 0.3%. An absolute calibration of the instrument was made by measuring the spectra of the gamma-rays from fluorine and lithium under proton bombardment and will be described in detail later. A magnet current of 50 amperes at 50 volts was required for the maximum field and this was supplied by a d.c. generator. The current was stabilized and controlled to an accuracy of within 0.1% by a feedback circuit operating on the field current of the generator.

The electron-positron pairs which were ejected predominantly normal to the foil by the gamma-rays were deflected through 180° by the magnetic field and detected by two sets of five Geiger counters placed in the plane of the foil. The counters were screened from direct gamma-radiation by the lead blocks.

These counters, which are described elsewhere (Rae 1950), were constructed from brass tube, $\frac{1}{2}$ in. in diameter and of $\frac{1}{32}$ in. wall thickness. The tube walls were cut away over 180° along their operating length and replaced by 0.001 in. copper foil to allow electrons or positrons to enter the counters with a minimum of scattering. The counter wires were supported on Kovar seals soldered to one end of the counter tubes. The other ends of the tubes were sealed up and provided with short helical springs which were located in blind holes recessed in the side plate of the spectrometer. The ends provided with Kovar seals projected through clearance holes in the other side plate of the spectrometer and were sealed to it with 'Q' compound. A gap of 1 in. was left between this plate and the magnet pole to allow connection to be made to the counters.

Baffles were placed in the vacuum chamber, as shown in Figure 2, to reduce the background due to electrons produced by gamma-rays from (n, γ) reactions in the counter walls and the lead shielding behind them, which could otherwise traverse the spectrometers and cause spurious coincidences.

(iv) Recording Equipment

The output pulses from the counters were fed via cathode followers and shaping circuits to twenty-five coincidence circuits each with a resolving time of about 2μ sec. The arrangement of these circuits is shown in the schematic diagram of Figure 2. The output pulses from the coincidence circuits were grouped into nine different energy channels, and the output of each channel was recorded on a mechanical counter.

The pulses from the monitor Geiger counter were recorded on a scale of 100. The output of this scaler was fed into a master control unit. This unit contained relays which switched on all the recording units and scalers simultaneously at the turn of a switch. It also contained a counter which could be preset to switch off all the recorders after any desired number of counts from the monitor counter scaler. Thus, all runs could be made for a fixed number of monitor counts. The time of each run was also recorded on a counter operating from a clock which gave pulses at half-second intervals.

§ 3. EXPERIMENTAL PROCEDURE

In measuring a particular gamma-ray spectrum a series of runs was made at a sequence of values of the magnetic field to cover the desired energy range. Each magnetic field setting gave counts in nine different energy channels, the spacing between channels corresponding to 5.8% of the H_p value of the centre channel. The interval between the successive values of the field was usually of the order of 10% or less, so that there was a considerable overlap between the runs. The results were then normalized for channel number and flux and plotted as a function of the mean H_p of a single particle. The precise energy of a particular gamma-ray was determined from the H_p value of the half-amplitude point on the high-energy side of the peak, as this could be measured more accurately than the H_p value of the peak itself and also should be less dependent upon the effects of scattering and energy loss in the foil. An analysis similar to that of Walker and McDaniel (1948) showed that a relation of the form $k = 600 H_p(1 + 2.5 \mu^2/k^2)$ should be accurate to within 0.5% over the energy range covered by this work, where k is the energy of the gamma-rays and μ the rest energy of an electron. No absolute calibration of the fluxmeter

coil was made. The spectra of the 6.13 mev. gamma-rays from the 340 kev. resonance of the reaction $^{19}\text{F}(p, \alpha, \gamma)^{16}\text{O}$ and of the 17.6 mev. gamma-rays from the 440 kev. resonance of the reaction $^7\text{Li}(p, \gamma)^8\text{Be}$ were measured and used to calculate the conversion factor between fluxmeter readings and $H\rho$ values. The values of the conversion factor so obtained from the two measurements differed by only 0.5% and the mean value was used in the calculation of subsequent results.

The spectrum of the 6.13 mev. gamma-rays from $^{19}\text{F}(p, \alpha, \gamma)^{16}\text{O}$ is shown in Figure 3 to illustrate the resolution of the spectrometer.

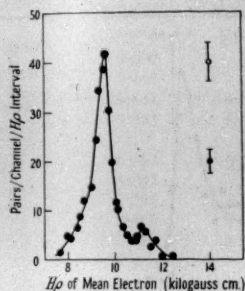


Figure 3. Spectrum of gamma-rays from $^{19}\text{F}(p, \alpha, \gamma)^{16}\text{O}$ at $E_p=340$ kev.

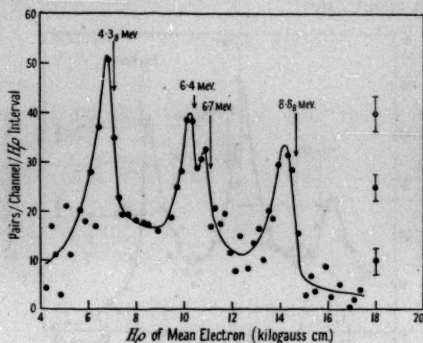


Figure 4. Gamma-rays from $\text{B}+\text{d}$ at $E_d=600$ kev.

§ 4. EXPERIMENTAL RESULTS

(i) The Reaction $\text{B}+\text{d}$

A target of natural boron was prepared on a brass plate and bombarded with 600 kev. deuterons. The measured gamma-ray spectrum is shown in Figure 4. At the time of this measurement the spectrometer had not been fitted with the baffles described in § 2 (iii) and the background coincidence rate due to neutrons was of the same order of magnitude as that due to pairs produced by gamma-rays in the foil. This background was subtracted to obtain the true spectrum shown in Figure 4, but, as a result, the statistical errors were rather large.

A target of ^{10}B , prepared in the Harwell electromagnetic separator, was then bombarded with 600 kev. deuterons and the consequent gamma-ray spectrum is shown in Figure 5. The background was considerably smaller on this run, partly because of the very much smaller neutron flux from the $^{10}\text{B}(\text{d}, \text{n})^{11}\text{C}$ reaction as compared with that from $^{11}\text{B}(\text{d}, \text{n})^{12}\text{C}$, and partly because of the baffles which had been fitted to the spectrometer. The gamma-ray yield was also greater because of the use of an isotopic target. The statistical accuracy was, therefore, very much better on this run than on the previous one.

A third run was then made with a target of separated ^{11}B under similar conditions and the gamma-ray spectrum is shown in Figure 6. The background on this run was of the order of magnitude of one third of the true coincidence rate at the peak of the spectrum and has been subtracted to give the spectrum shown.

The results of these three runs are summarized in Table 1, together with the measurements of previous workers on the same reaction. It will be seen that the majority of high energy gamma-rays from B+d reactions are due to the ^{10}B isotope and that $^{11}\text{B}+\text{d}$ does not produce any gamma-rays of energy greater than 4.44 MeV. The spectrum from $^{10}\text{B}+\text{d}$ is clearly complex in the region between 6 and 7 MeV, and is not completely resolved. However, both the B+d and $^{10}\text{B}+\text{d}$ runs indicate two gamma-rays of the same order of intensity at 6.4 and 6.7 MeV. There is also a pronounced 'tail' on the high-energy side of these peaks which suggests the presence of a gamma-ray of smaller intensity at about 7 MeV.

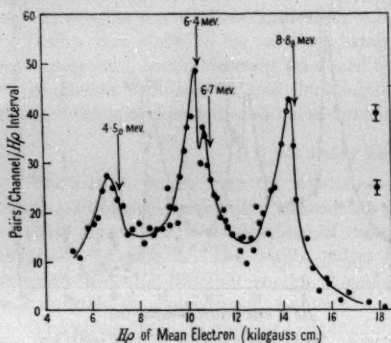
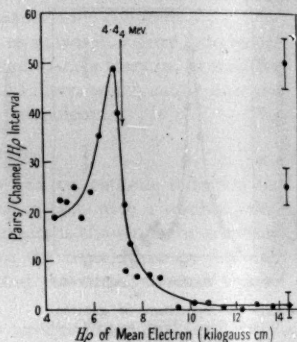
Figure 5. Gamma-rays from $^{10}\text{B}+\text{d}$ at $E_d=600$ kev.Figure 6. Gamma-rays from $^{11}\text{B}+\text{d}$ at $E_d=600$ kev.

Table 1. Summary of Gamma-ray Measurements

Reaction	Present work		Gaertner <i>et al.</i> (1939)		Halpern and Crane (1939)	
	E_γ (MeV.)	Rel. int.	E_γ (MeV.)	Rel. int.	E_γ (MeV.)	Rel. int.
B+d	8.88 ± 0.06	1	9.1 ± 0.4	1	8.6	1
	6.7 ± 0.15	0.8	6.9 ± 0.4	3	6.0	2
	6.4 ± 0.15	0.9			4.2	6
	4.38 ± 0.05	2.9	4.4 ± 0.3	10		
$^{10}\text{B}+\text{d}$	8.88 ± 0.06	1				
	6.7 ± 0.15	0.8				
	6.4 ± 0.15	1.0				
	4.50 ± 0.05	0.9				
$^{11}\text{B}+\text{d}$	4.44 ± 0.05					
$^{27}\text{Al}+\text{p}$	12.12 ± 0.1	1				
	10.46 ± 0.07	7.5				
	7.62 ± 0.1	3.5				

We can now consider the interpretation of these results. In the case of $^{10}\text{B}+\text{d}$, three reactions are energetically possible as shown in the energy level diagram, Figure 7(a) (Hornyak *et al.* 1950). These are $^{10}\text{B}(\text{d}, \text{p})^{11}\text{B}$, $Q=9.24$ MeV.; $^{10}\text{B}(\text{d}, \alpha)^8\text{Be}$, $Q=17.81$ MeV. and $^{10}\text{B}(\text{d}, \text{n})^{11}\text{C}$, $Q=6.53$ MeV.

The reaction $^{10}\text{B}(d, p)^{11}\text{B}$ leads to a number of excited states in ^{11}B . The most precise measurements of the energies of these proton groups have been made by Buechner and his co-workers using 1.5 mev. deuterons and his results are shown in Table 2, taken from the recent review by Hornyak *et al.* (1950).

Table 2. Energy Levels of ^{11}B from the $^{10}\text{B}(d, p)^{11}\text{B}$ Reaction

Proton measurements			Gamma-rays	
Buechner (1950)	Rutherglen and Smith		Present work	
E (level) (mev.)	E (level) (mev.)	Rel. int.	E_γ (mev.)	Rel. int.
0.000				
2.141				
4.457	4.50	1.9	4.50	0.9
5.033	5.01	0.3		
			6.4	1.0
6.752	6.72	2.1	6.7	0.8
6.802				
7.297	7.26	0.5		
8.565	8.51	0.1		
8.921	8.93	1.0	8.88	1.0

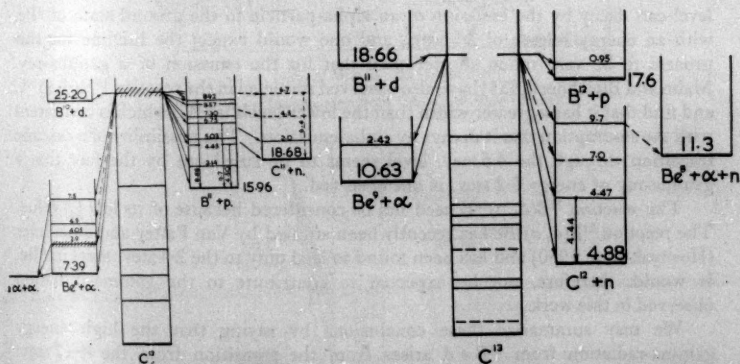


Figure 7(a). Energy level diagram for $^{10}\text{B} + d$.

Figure 7(b). Energy level diagram for $^{11}\text{B} + d$.

We also include in Table 2 the results of measurements on the relative intensity of some of these proton groups obtained with a magnetic spectrometer in this laboratory (Rutherglen and Smith, to be published) using 600 kev. deuterons. It will be seen that the energies of the measured gamma-rays at 4.5, 6.7 and 8.9 mev. are in good agreement with the energy levels predicted by the three most intense proton groups. The intensities of the remaining proton groups are too small to give observable gamma-rays in this work, but the proton group corresponding to the 7.3 mev. level may be responsible for the shape of the gamma-ray spectrum on the high energy side of the 6.7 mev. peak.

The $^{10}\text{B}(d, \alpha)^8\text{Be}$ reaction is known to lead to levels in ^8Be at 7.5 mev. and 2.9 mev. (Smith and Murrell 1939) but it is almost certain that these levels decay

with the emission of two alpha-particles and would not, therefore, contribute to the observed gamma-radiation.

The neutrons from $^{10}\text{B}(\text{d}, \text{n})^{11}\text{C}$ have been studied by Gibson (1949) at $E_d = 0.93$ mev. and by Swann and Hudspeth (1949) at $E_d = 1.4$ mev. The former find neutron groups corresponding to the ground state and to a 2.0 mev. excited state in ^{11}C . The latter find evidence for only two levels in ^{11}C at 4.5 mev. and 6.7 mev., but there is a possibility that the corresponding neutron groups were due to contamination. If a level exists in the region of 6.7 mev. it may be responsible for the complexity of the gamma-ray spectrum observed in this region.

We may summarize these reactions by saying that the majority of the high energy radiation from $^{10}\text{B} + \text{d}$ arises from transitions between excited states of ^{11}B and the ground state, following the $^{10}\text{B}(\text{d}, \text{p})^{11}\text{B}$ reaction, but that there may be some gamma-radiation of energy about 6.4 mev. from the $^{10}\text{B}(\text{d}, \text{n})^{11}\text{C}$ reaction.

In the case of $^{11}\text{B} + \text{d}$, we must consider the reactions $^{11}\text{B}(\text{d}, \text{n})^{12}\text{C}$, $Q = 13.78$ mev.; $^{11}\text{B}(\text{d}, \text{p})^{12}\text{B}$, $Q = 1.1$ mev. and $^{11}\text{B}(\text{d}, \alpha)^8\text{Be}$, $Q = 8.03$ mev., as shown in the energy level diagram of Figure 7 (b) (Hornyak *et al.* 1950). The first reaction has recently been studied by Gibson (1949) and is found to yield neutron groups leading to excited states of ^{12}C at 9.72 ± 0.15 mev. and 4.47 ± 0.10 mev. with relative intensities of 0.67 : 1. The second group corresponds well with the gamma-ray energy of 4.44 ± 0.05 mev. measured in this work. However, there is no evidence of a gamma-ray at 9.7 mev. This is not unexpected, since this level can decay by the emission of an alpha-particle to the ground state of ^8Be , with an energy release of 2.3 mev., and one would expect the lifetime for this process to be very much shorter than that for the emission of a gamma-ray. Malm and Buechner (1951) have also observed this level in the reaction $^{15}\text{N}(\text{d}, \alpha)^{12}\text{C}$ and find that it has a greater width than the lower levels in ^{12}C , which is consistent with the assumption that it decays by alpha-emission. The possibility of a cascade transition through the 4.5 mev. level seems to be ruled out by the fact that a gamma-ray of energy 5.2 mev. is not observed.

The reaction $^{11}\text{B}(\text{d}, \text{p})^{12}\text{B}$ need not be considered because of its low Q -value. The reaction $^{11}\text{B}(\text{d}, \alpha)^8\text{Be}$ has recently been studied by Van Patter and Buechner (Hornyak *et al.* 1950) and has been found to lead only to the 2.4 mev. level in ^8Be . It would, therefore, not be expected to contribute to the gamma-radiation observed in this work.

We may summarize these conclusions by saying that the high energy gamma-radiation from $^{11}\text{B} + \text{d}$ arises from the transition from the 4.47 mev. level in ^{12}C to the ground state and that the 9.7 mev. level in ^{12}C decays by alpha-particle emission to ^8Be .

(ii) The Reaction $^{27}\text{Al} + \text{p}$

The measured gamma-ray spectrum from a thick aluminium target bombarded with 750 kev. protons is shown in Figure 8. The energies and relative intensities of the main peaks are shown in Table 1. The thin target excitation curve of the gamma-rays from $\text{Al} + \text{p}$ has been measured by a number of workers and shows a number of sharp resonances. In order to obtain sufficient intensity in the present work it was necessary to use a thick target, so that all the resonances below 750 kev. were excited. Even so, the total gamma-ray yield was only about one-fifteenth of that produced by the 340 kev. resonance of $^{19}\text{F}(\text{p}, \alpha, \gamma)^{16}\text{O}$. It will be seen that three gamma-rays of energies

12.12 ± 0.1 mev., 10.46 ± 0.07 mev., and 7.62 ± 0.1 mev. are clearly resolved, but the background both above and below the 7.6 mev. peak suggests the presence of other weak gamma-rays. The low intensity of the reaction prevented a more detailed investigation of this region.

The interpretation of these gamma-rays can be discussed in terms of the energy level diagram of ^{28}Si shown in Figure 9. The only reactions which are

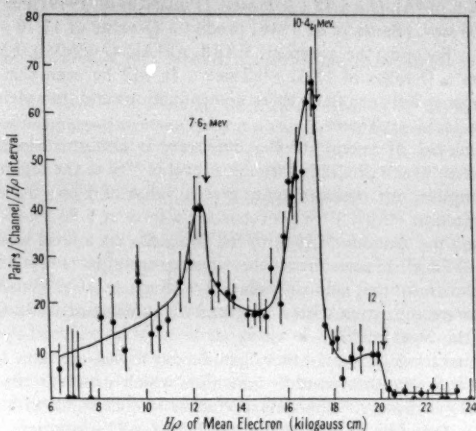


Figure 8. Gamma-rays from $^{27}\text{Al} + p$ at $E_p = 750$ kev.

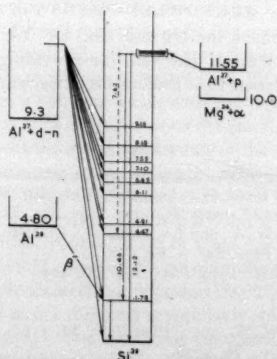


Figure 9. Energy level diagram for $^{27}\text{Al} + p$.

energetically possible in this case are $^{27}\text{Al}(p, \gamma)^{28}\text{Si}$ and $^{27}\text{Al}(p, \alpha)^{24}\text{Mg}$ and only the former has a sufficiently large Q -value to produce the observed gamma-rays. The most energetic gamma-ray is presumed to correspond to the direct transition to the ground state of ^{28}Si . From the results of Brostrom *et al.* (1947) on the relative intensities of the resonances below our bombarding energy of 750 kev.

we assume the mean effective bombarding energy to be 630 kev., which corresponds to an additional excitation energy of 610 kev. in centre-of-mass coordinates. Although it is known that the spectrum is not identical for all resonances (Tangen 1946), the above assumption cannot be in error by more than ± 100 kev. We thus obtain a value of 11.51 ± 0.2 mev. for the Q -value of the ground state transition. This Q -value may be calculated by two other methods. First, the reactions $^{27}\text{Al}(d, p)^{28}\text{Al}$, $Q = 5.45 \pm 0.05$ mev. (Pollard *et al.* 1949) and $^{28}\text{Al}(\beta^-)^{28}\text{Si}$, $Q = 4.80 \pm 0.05$ mev. (Benes *et al.* 1948) predict a Q -value of 11.70 ± 0.1 mev. for $^{27}\text{Al}(p, \gamma)^{28}\text{Si}$. Second, the reaction $^{27}\text{Al}(d, n)^{28}\text{Al}$, $Q = 9.08 \pm 0.2$ mev. (Peck 1949) predicts a Q -value of 11.31 ± 0.2 mev. It will be seen that there is no serious discrepancy between these three determinations and they yield a weighted mean value of 11.55 ± 0.07 mev.

The gamma-ray of energy 10.46 ± 0.07 mev. is almost certainly due to a cascade transition which proceeds through a level of ^{28}Si in the region of 1.8 mev. On this assumption our measurements give a value of 1.66 ± 0.2 mev. for this level. The reaction $^{28}\text{Al}(\beta^-)^{28}\text{Si}$ proceeds via a level at 1.80 ± 0.05 mev. (Benes *et al.* 1948) and the reaction $^{27}\text{Al}(d, n)^{28}\text{Si}$ proceeds via a level which has been measured as 1.78 ± 0.13 mev. from the neutron groups (Peck 1949) and as 1.72 ± 0.08 mev. from the gamma-radiation (Alburger 1949). Thus, all the determinations are consistent with a weighted mean value of 1.75 ± 0.04 mev. for the energy of this level in ^{28}Si .

The interpretation of the 7.6 mev. gamma-ray is less certain, but it seems probable that it is due to a cascade transition which proceeds through a level in ^{28}Si at 4.50 ± 0.15 mev. This interpretation is consistent with the level at 4.47 ± 0.13 mev. found by Peck (1949) in the $^{27}\text{Al}(d, n)^{28}\text{Si}$ reaction.

ACKNOWLEDGMENTS

The authors wish to thank the Director and Dr. W. D. Allen of the Atomic Energy Research Establishment, Harwell, for providing the separated isotopic targets of boron, and Professor P. I. Dee for his advice and encouragement during the course of the work.

REFERENCES

- ALBURGER, D. E., 1949, *Phys. Rev.*, **75**, 51.
 BENES, J., HEDGRAN, A., and HOLE, N., 1948, *Ark. Mat. Astr. Fys.*, **35A**, No. 12.
 BROSTROM, K. J., HUUS, T., and TANGEN, R., 1947, *Phys. Rev.*, **71**, 661.
 GAERTTNER, E. R., FOWLER, W. A., and LAURITSEN, C. C., 1939, *Phys. Rev.*, **55**, 27.
 GIBSON, W. M., 1949, *Proc. Phys. Soc. A*, **62**, 586.
 HALPERN, J., and CRANE, H. R., 1939, *Phys. Rev.*, **55**, 415.
 HORNYAK, W. F., LAURITSEN, T., MORRISON, P., and FOWLER, W. A., 1950, *Rev. Mod. Phys.*, **22**, 291.
 MALM, R., and BUECHNER, W. W., 1951, *Phys. Rev.*, **81**, 519.
 PECK, R. A., 1949, *Phys. Rev.*, **76**, 1279.
 POLLARD, E. C., SAILOR, V. L., and WYLY, L. D., 1949, *Phys. Rev.*, **75**, 725.
 RAE, E. R., 1950, *J. Sci. Instrum.*, **27**, 143.
 RAE, E. R., RUTHERGLEN, J. G., and SMITH, R. D., 1950, *Proc. Phys. Soc. A*, **63**, 775.
 SMITH, C. L., and MURREL, E. B. M., 1939, *Proc. Camb. Phil. Soc.*, **35**, 298.
 SWANN, C. P., and HUDSPETH, E. L., 1949, *Phys. Rev.*, **76**, 168.
 TANGEN, R., 1946, *K. Norske Vidensk. Selsk. Skr.*, No. 1.
 WALKER, R. L., and MCDANIEL, B. D., 1948, *Phys. Rev.*, **74**, 315.

The Density of the Penetrating Particles in Extensive Cosmic-Ray Air Showers

By C. B. A. McCUSKER AND D. D. MILLAR

Dublin Institute for Advanced Studies

MS. received 25th May 1951 ; read at Science meeting in Belfast 6th July 1951

ABSTRACT. The ratio of penetrating particles to electrons in extensive cosmic-ray showers has been investigated experimentally at sea level. For the great majority of showers this ratio, in agreement with previous results, is found to be 2.5%. A small number of showers was detected in which the proportion of penetrating particles was much greater.

§1. INTRODUCTION

IT is well known that the particles of the extensive air showers consist predominantly of electrons but that there is also present a small fraction of more penetrating particles. The ratio k of the density of penetrating particles to electrons has been found to be of the order of 2% (see §6 for references), but evidence for a variation in k has also been found within a limited range of k values (Coconi, Tongiorgi and Greisen 1949 a, b). The present experiment was carried out in order to detect such variations if they exist over a wider possible range of values.

§2. THE EXPERIMENTAL ARRANGEMENT

Three trays of ten Geiger-Müller counters, of area $1,750 \text{ cm}^2$, were situated at the vertices of a triangle of side 5 metres, housed in a wooden hut 4 metres below a roof of mean thickness 5 gm/cm^2 . For the greater part of the experiment these trays were shielded by 20 cm. Pb above, with 15 cm. Pb at the ends and sides and 2.5 cm. Pb below. When a run was made with the trays unshielded, they were placed above the lead piles with a layer of wood 8.5 cm. thick between the counters and the lead to avoid a possible spurious increase of the density of the particles at the counters by back scattering from the lead. When unshielded, the counters were covered by an aluminium box 1 mm. thick.

In addition to these three trays which provided a threefold coincidence as master pulse, an array of six counter trays of areas $1,400 \text{ cm}^2$, 700 cm^2 , 350 cm^2 , 175 cm^2 , 80 cm^2 and 37 cm^2 , enclosed in an aluminium box 1 mm. thick, was situated within the triangle formed by the master trays. The four largest of these trays consisted of 8, 4, 2 and 1 counters respectively, identical with the counters comprising the master trays. The remaining two consisted of single counters of smaller size. All the counters were separated from each other by 0.5 cm. Each of the six counter trays was connected to a neon lamp in a hodoscope so that by examination of the photographic records it could be determined which of the hodoscope trays had been struck by each of the extensive showers detected by the three master trays.

The resolving time of the threefold coincidence circuit providing the master pulse was 0.6 microsecond so that in the total time of recording less than one casual coincidence would be expected.

§3. ANALYSIS OF THE HODOSCOPE DATA

(i) *Notation*

It is convenient to consider one fortieth of the area of the master trays as the unit of area in analysing the hodoscope results. The areas of the hodoscoped trays are then 32, 16, 8, 4, 1.8 and 0.85 units, while the master trays are 40 units of area. For ease in calculation the areas of the two smallest hodoscoped trays were taken as 2 and 1 units. Errors involved by this approximation will be negligible. It will be observed that any combination of the hodoscoped trays set off in coincidence with the three master trays may then be denoted uniquely by one of the integers from 0 to 63. For example, a coincidence in which none of the hodoscoped trays is struck is denoted by '0', one in which all the trays are discharged by '63'; a '48' coincidence is one in which trays of areas 32 and 16 only are set off and no others, and so on.

The numbers of coincidences recorded involving the various possible combinations of the unshielded hodoscoped trays will be given in the following two sections, with the shielded and the unshielded master trays respectively providing the shower selection. The observed distribution of the numbers of different types of coincidences will be compared with the predicted distributions.

(ii) *The Shielded Distribution*

The expected counting rate of any arrangement of counters may be calculated using the well-known integrals (Broadbent and Jánosy 1948). This calculation is based on the following assumptions: (i) that the average particle density in a given shower is constant over the experimental arrangement, (ii) that the spatial distribution of particles is purely random, (iii) that the rate of incidence of showers with particle density equal to or greater than x per unit area is $N(x) = Bx^{-\gamma}$, γ and B being constants, and (iv) that k , the ratio of penetrating particles to electrons, is a constant.

In Table 1, column 2, are given the observed numbers of coincidences involving the particular combination of the hodoscoped trays indicated in column 1. In the succeeding columns the calculated distributions of the various events, normalized to the observed total number, are given using the density exponent $\gamma = 1.425$ as found by Broadbent, Kellermann and Hakeem (1950) and for the values of k indicated.

The combinations given in Table 1 are those of which two or more instances were recorded. It will be observed that there were seven other combinations which occurred to the extent of once each. These have been grouped together in the category 'others' and are compared with the predicted numbers of events other than those listed.

In order to find the calculated distribution which best fits the observed distribution, we evaluate the sum of the squares of the deviations of the observed numbers of events o_i of the different types tabulated from the corresponding calculated numbers c_i . Thus $u^2 = \sum (o_i - c_i)^2$. We may consider the best agreement to be afforded by that calculated distribution for which u^2 is a minimum. It will be seen from the values of u^2 given in the last line of the Table that a minimum is reached corresponding to the calculated distribution for $k = 2.5/40 = 6.25\%$. The expected value of u^2 is given by $\bar{u}^2 = N - Q/N$ where N is the total number of events recorded and $Q = \sum c_i^2$. For a single observed distribution differing from the

predicted distribution only because of statistical fluctuation of the individual numbers of the events recorded, the deviation σ of u^2 from the expected value $\overline{u^2}$ has the mean square value $\overline{\sigma^2}$ given by*

$$\frac{1}{2}\overline{\sigma^2} = \frac{1}{2}(\overline{u^2} - \overline{u^2})^2 = \left(1 - \frac{1}{N}\right)Q + \left(1 - \frac{3}{N}\right)\frac{Q^2}{N^2} - \left(1 - \frac{2}{N}\right)\frac{2K}{N}$$

where $K = \Sigma c_i^3$. Thus for the observed distribution to be in agreement with the

Table 1. Shielded Distribution

Counter combination	No. of events	Values of k							
		0.5 40	1.0 40	1.5 40	2.0 40	2.5 40	3.0 40	5.0 40	40 40
'63'	122	286	221	175	143	120	102	62	4
'62'	53	44	67	75	77	76	73	58	7
'61'	16	11	19	23	25	26	25	21	3
'60'	48	14	26	36	42	47	50	54	14
'58'	5	5	7	11	13	15	17	19	6
'57'	7	3	3	5	6	6	7	8	3
'56'	29	2	9	14	20	25	29	40	26
'54'	2	1	1	2	3	4	4	5	2
'50'	4	1	2	2	3	4	4	6	5
'48'	20	3	4	6	9	11	14	23	43
'44'	2	0	0	1	1	2	2	3	4
'40'	7	1	1	2	2	3	4	7	17
'36'	3	0	1	1	1	1	2	3	8
'32'	13	0	1	2	4	5	6	12	61
'16'	7	0	0	1	1	1	2	4	24
'12'	2	0	0	0	0	0	0	0	1
'0'	26	0	1	1	2	3	4	7	87
'others'	7	4	10	15	21	24	29	41	60
Total	373								

$$u^2 = 30,165 \quad 12,046 \quad 4,831 \quad 2,326 \quad 1,778 \quad 2,125 \quad 5,558 \quad 27,175$$

Table 2. Unshielded Distribution

(1)	(2)	(3)	(1)	(2)	(3)
'63'	9	12	'40'	46	51
'62'	31	20	'36'	14	23
'61'	16	8	'34'	8	11
'60'	60	41	'32'	182	180
'58'	25	17	'24'	12	17
'57'	10	8	'20'	7	8
'56'	88	78	'16'	71	70
'54'	3	6	'12'	4	3
'52'	30	32	'8'	33	31
'50'	14	15	'4'	9	15
'48'	131	128	'others'	48	62
'44'	7	11	'0'	246	257

Total 1,104; $u^2 = 1,266$; expected value $\overline{u^2} = 979 + 460$

(1) Counter combination; (2) observed number of events; (3) calculated number of events.

* We are indebted to Professor Schrödinger for his investigation of the statistical problem here involved and for making available to us this expression.

calculated distribution with $k=6.25\%$ one expects u^2 to be within the range $\overline{u^2} \pm (\sigma^2)^{1/2} = 307 \pm 182$. In fact we find $u^2 = 1,778$ for this case hence, while $k=6.25\%$ may give the best agreement with the observed distribution, this agreement is unsatisfactory and, therefore, at least one of the initial assumptions (i) and (iv) used in the derivation of the calculated distributions cannot be strictly valid.

(iii) The Unshielded Distribution

Table 2 gives the observed and calculated values for the unshielded rates; it includes all combinations of which five or more instances occurred. As before the sum of the squares of the deviations was evaluated. The expected value is $\overline{u^2} \pm (\sigma^2)^{1/2} = 979 \pm 460$, and observed value $u^2 = 1,266$. Agreement between the observed and calculated distributions in this case therefore is satisfactory.

§ 4. THE THREEFOLD COINCIDENCE RATES

It is possible to obtain the fraction k by a number of different methods. One method has already been discussed. Other methods are to compare the rates of threefold coincidences of various combinations of shielded and unshielded trays. The three combinations used were (a) threefold unshielded, (b) two unshielded and one shielded, (c) threefold shielded, and the number of coincidences per hour observed were

$$(a) R_{3U} = 33.9 \pm 0.97, (b) R_{2U+1S} = 2.36 \pm 0.10, (c) R_{3S} = 0.1159 \pm 0.0057.$$

The rates (a) and (b) have been corrected for barometric variations to the mean atmospheric pressure over the run (c), using a barometer coefficient of -11% per cm. Hg which is known to apply to observations with counter arrangements (a) and (b) (Millar 1950, 1951). From any two of the counting rates given above a value of k can be deduced. The values so obtained are as follows: from (b) and (a), $k = 2.55 \pm 0.10\%$, from (c) and (a), $k = 1.86 \pm 0.07\%$, from (c) and (b), $k = 1.1 \pm 0.3\%$. It will be seen that these three values of k differ markedly, and even considering the first two values as two independent determinations of k , the difference between them is greater than can be explained by statistical fluctuation of the counting rates alone. Moreover, none of these values is in agreement with the value, 6.26% , giving the best agreement with prediction for the hodoscope data with the three shielded trays.

The reason for these discrepancies must be sought in the original assumptions (i) to (iv) which provide the basis of the calculations, and these assumptions will be examined in the light of the observed data.

§ 5. DISCUSSION OF THE EXPERIMENTAL RESULTS

(i) Unshielded Data

A calculation of the average densities triggering the different combinations shows that the range of densities (3 to 400 particles per square metre) is much the same as that investigated by Broadbent *et al.* (5 to 500 particles per square metre). It will be seen that the predicted and observed rates are in satisfactory agreement when Broadbent's value for γ is used.

There is some evidence that the observed number of high density events is larger than the calculated number. If this effect is genuine (none of the individual fluctuations is greater than 2.5 times the expected deviation) it is probably due to the variation of the shower density over the apparatus as suggested by the authors mentioned.

(ii) *Shielded Data*

The great majority of the showers falling on the apparatus have a mean value of $k = 2.55 \pm 0.10\%$. During the total running time with the three shielded trays about 100,000 showers capable of triggering the three unshielded trays fell on the apparatus. Of these 373 triggered the shielded arrangement and it is of these showers that a significant proportion show variations in k .

The most significant difference between the predicted and calculated rates is that for the '0' events. Twenty-six showers were observed in which three shielded trays were discharged without an accompanying discharge of any of the unshielded trays. In a further thirteen events only the largest of the unshielded trays was struck. It would appear that these showers can only be explained by assuming a value of k of $\frac{1}{2}$ to 1.

Considering now the high density end of Table 1 it will be seen that 122 events were recorded in which all trays were discharged. If k is equal to 2.5% one expects 330 such events to be recorded. (The threefold shielded coincidence rate must be increased by 50%, from 0.116 to 0.174 per hour, to bring it into agreement with the threefold unshielded rate for $k = 2.5\%$.) The average density here involved is greater than 1,000 particles per square metre and it is therefore possible that in this density region k is less than 2.5% or that γ is greater than 1.425, both of which variations would lead to the recording of fewer high density showers than are expected for k constant and γ having these values. However, it is also possible that for such high densities the variation of the density of incident showers over the apparatus becomes more important.

§6. COMPARISON WITH PREVIOUS EXPERIMENTS

Previous determinations of the value of k have in general involved one of two methods: (a) the comparison of the coincidence rate obtained from unshielded counters with the rate obtained from unshielded counters plus one or more shielded counters in coincidence, or (b) the comparison of the coincidence rates obtained with all counters unshielded and with all counters shielded. Using the first method Broadbent and Jánossy (1948), Chowdhuri (1948) and Cocconi, Tongiorgi and Greisen (1949a) obtain at sea level a value of k of approximately 2.5% which is in good agreement with our value obtained by the same method, i.e. comparing the twofold unshielded plus one shielded rate with the threefold unshielded rate. At about 3,000 metres altitude both methods have been used, the first by Cocconi, Tongiorgi and Greisen (1949a), and the second by Treat and Greisen (1948) and Ise and Fretter (1949). As pointed out by Ise and Fretter the second method appears to give a higher value of k than the first. This is in direct contradiction to our results, since we obtain a lower value of k from the second method (comparing our threefold shielded and threefold unshielded rates) than from the first. The results at high altitude, however, were obtained from experimental arrangements involving different areas, separations and dispositions of the counters and comparison of these results is complicated by this fact.

Evidence that k is not constant but varies with the mean electron density to which an arrangement of counters responds has been deduced by Cocconi, Tongiorgi and Greisen (1949a) who find that k is proportional to $\bar{x}^{-0.13}$. The problem of the variation of k in relation to the lateral spread of the showers has also been investigated by these authors. They find that at each of two distances of 48 m. and 96 m. from the shower core detected by a 'core selector' there is no

evidence that k is not constant for electron densities over a range varying by a factor of more than 100; there is evidence, however, that k increases with distance from the shower core and they deduce that the value may be twice as great at 100 m. from the core as it is at 5 m., a result which is in agreement with the weak dependence of k upon the mean particle density previously detected by these authors.

Such a slow variation of k with distance from the shower core could explain the discrepancies in Table 1 for the high density regions corresponding to showers detected near the core. The discrepancies in the low density regions, however, cannot be satisfactorily explained in the same way in terms of the lateral structure of the showers since, in particular, our observed '0' events must arise from shower regions in which the density of penetrating particles is at least of the same order of magnitude as the density of the accompanying electrons. We are led therefore to interpret our low density events in terms of the longitudinal structure of the extensive air showers and conclude that with an arrangement of three shielded counters in coincidence an appreciable fraction of the recorded coincidences are due to extensive air showers in which the soft component has been largely absorbed in the atmosphere before reaching the apparatus, leaving only an extended tail consisting of non-interacting penetrating particles and, presumably, their accompanying knock-on electrons.

§ 8. CONCLUSION

It has been shown that the assumption of constant k is invalid from analysis of the extensive penetrating shower data here obtained. It is possible to interpret these results on the basis that the majority of showers have a mean value of $k=2.5\%$, but it is also necessary to postulate that there exists a small number of showers with k approaching unity. If these are in fact the tail ends of extensive air showers whose soft component has died out above the apparatus as seems likely, it would lend support to the hypothesis that all cosmic-ray particles observed in the lower atmosphere are indeed parts of extensive air showers as recently suggested by Cocconi (1950).

ACKNOWLEDGMENTS

We wish to thank Professor E. Schrödinger for considerable help and advice on the statistical problem, Dr. T. E. Nevin for the loan of small counters and Drs. J. G. Wilson and G. D. Rochester for comment. We are indebted to Miss E. Smith who carried out the numerical computation. One of us (D.D.M.) is grateful to the Sir James Caird's Travelling Scholarships Trust for the provision of a Scholarship.

REFERENCES

- BROADBENT, D., and JÁNOSSY, L., 1948, *Proc. Roy. Soc. A*, **192**, 364.
 BROADBENT, D., KELLERMANN, E. W., and HAKEEM, M. A., 1950, *Proc. Phys. Soc. A*, **63**, 864.
 CHOWDHURI, B. 1948, *Nature*, Lond., **161**, 680.
 COCCONI, G., 1950, *Phys. Rev.*, **79**, 1006.
 COCCONI, G., COCCONI-TONGIORGI, V., and GREISEN, K., 1949 a, *Phys. Rev.*, **75**, 1063; 1949 b, *Ibid.*, **76**, 1020.
 ISE, J., and FRETTER, W. B., 1949, *Phys. Rev.*, **76**, 933.
 MILLAR, D. D., 1950, *Proc. Roy. Irish. Acad.*, **A**, **54**, 115; 1951, *Nuovo Cimento*, **8**, 279.
 TREAT, J. E. and GREISEN, K., 1948, *Phys. Rev.*, **74**, 414.

The Diamagnetic Anisotropy of Large Aromatic Systems: III Structures with Hexagonal Symmetry

By R. McWEENY

Laboratories of Physical Chemistry and Coke Research, University of Durham,
King's College, Newcastle-upon-Tyne

Communicated by C. A. Coulson; MS. received 30th April 1951

ABSTRACT. The molecular orbital method is employed in calculations of the diamagnetic anisotropies of a series of highly condensed aromatic systems having hexagonal symmetry and containing up to fifty-four carbon atoms. A new method of calculation is introduced in which the π -electron susceptibility of the whole molecule is determined by an integration, no knowledge of the unperturbed energy levels being necessary: the inclusion of overlap between adjacent atomic orbitals is shown generally to have little effect on the calculations.

The results are compared with those calculated using the method of Pauling: this semi-classical method is found to be quite misleading when applied to large molecules or to molecules possessing stray C-C bonds. Qualitative valence bond considerations are advanced in support of these conclusions, and certain general results are tentatively suggested.

§1. REDUCTION OF THE SECULAR EQUATION: AN EXAMPLE

IN this paper the method of molecular orbitals is employed, in the manner outlined in Part I and illustrated in Part II of an earlier paper (McWeeny 1951, to be referred to as I and II), in a calculation of the diamagnetic anisotropy of various carbon structures containing as many as 54 carbon atoms. The secular equations involved in calculations of this type cannot often be dealt with by analytical methods (cf. II) but they can be made manageable in certain cases of high molecular symmetry by an application of group theory: for this reason our attention will here be confined to structures possessing hexagonal symmetry, in which case a great simplification can be achieved. An application to the benzene molecule affords an excellent example of the method to be used; we shall therefore consider this case in some detail, although the results (obtained otherwise) are well known (e.g. London 1937).

The point group of the benzene molecule *with a magnetic field along the 6-fold axis* is the cyclic group C_6 , the reduction of symmetry from the normal D_{6h} resulting from the exclusion of reflections by the field (cf. I, Appendix I). The character table for C_6 is given below.

	$E (= C^6)$	C	C^2	C^3	C^4	C^5
$\Gamma_1 \quad \chi_1$	1	1	1	1	1	1
$\Gamma_2 \quad \chi_2$	1	-1	1	-1	1	-1
$\Gamma_3 \quad \chi_3$	1	ω	ω^2	ω^3	ω^4	ω^5
$\Gamma_4 \quad \chi_4$	1	ω^5	ω^4	ω^3	ω^2	ω
$\Gamma_5 \quad \chi_5$	1	ω^2	ω^4	1	ω^3	ω^4
$\Gamma_6 \quad \chi_6$	1	ω^4	ω^2	1	ω^4	ω^2

.....(1)

Since the group is Abelian, an irreducible representation by unitary matrices is necessarily unidimensional: consequently the representative 'matrices' $D_r(s)$ (s being a group operation and r denoting the r th representation, Γ_r) are synonymous with the characters $\chi_r(s)$ given above.

In constructing molecular orbitals from the atomic 2p orbitals $\phi_1, \dots, \phi_6$ of the six carbon atoms it is possible to write down immediately six distinct linear combinations providing a basis adapted to the complete decomposition of the six-dimensional (ϕ -space) representation into the direct sum of six one-dimensional representations. For, from above, these combinations, $\psi_1, \dots, \psi_6$, say, (ψ_r being the basis vector for the invariant (uni-dimensional) sub-space providing the representation Γ_r) must transform under the operations of the group according to $\psi_r \rightarrow \psi_r' = \chi_r(s)\psi_r$. Here s is regarded as a coordinate transformation leaving the Hamiltonian invariant and ψ_r' is the function constructed in the rotated coordinate system by the same process as ψ_r is constructed in the original system.

Now if we take $\psi_r = \sum_m \chi_r(C^m)\phi_m$

$$\begin{aligned} \text{we have } \chi_r(C')\psi_r &= \sum_m \chi_r(C')\chi_r(C^m)\phi_m = \sum_m \chi_r(C^{l+m})\phi_m \\ &= \sum_n \chi_r(C^n)\phi_{n-l} = \sum_m \chi_r(C^m)\phi_{m-l} = \psi_r' \end{aligned}$$

where ψ_r' is constructed in the frame where ϕ_m is replaced by ϕ_{m-l} , i.e. rotated by C^l ; ψ_r therefore transforms under all operations C^l in the way required of a basis function for the r th representation.

The basis functions for the completely reduced representation are thus

$$\left. \begin{aligned} \Gamma_1 \quad \psi_1 &= \frac{1}{\sqrt{6}}(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6) \\ \Gamma_2 \quad \psi_2 &= \frac{1}{\sqrt{6}}(\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6) \\ \Gamma_3 \quad \psi_3 &= \frac{1}{\sqrt{6}}(\phi_1 + \omega\phi_2 + \omega^2\phi_3 + \omega^3\phi_4 + \omega^4\phi_5 + \omega^5\phi_6) \\ \Gamma_4 \quad \psi_4 &= \frac{1}{\sqrt{6}}(\phi_1 + \omega^5\phi_2 + \omega^4\phi_3 + \omega^3\phi_4 + \omega^2\phi_5 + \omega\phi_6) \\ \Gamma_5 \quad \psi_5 &= \frac{1}{\sqrt{6}}(\phi_1 + \omega^2\phi_2 + \omega^4\phi_3 + \phi_4 + \omega^2\phi_5 + \omega^4\phi_6) \\ \Gamma_6 \quad \psi_6 &= \frac{1}{\sqrt{6}}(\phi_1 + \omega^4\phi_2 + \omega^2\phi_3 + \phi_4 + \omega^4\phi_5 + \omega^2\phi_6) \end{aligned} \right\} \dots\dots (2)$$

In the absence of the field the representations Γ_3, Γ_4 and Γ_5, Γ_6 are equivalent to two pairs of degenerate representations but this degeneracy is removed by the field (I, Appendix I).

Using the fact that the only non-vanishing matrix elements of the Hamiltonian are those between vectors whose direct products provide a basis for a representation containing the totally symmetric Γ_1 , the usual secular equation of a m.o. treatment based on $\psi_1, \dots, \psi_6$ becomes

$$\begin{vmatrix} \alpha + 2\mathcal{R}(\beta') - E & & & & & \\ & \alpha + 2\mathcal{R}(-\beta') - E & & & & \\ & & \alpha + 2\mathcal{R}(\omega\beta') - E & & & \\ & & & \alpha + 2\mathcal{R}(\omega\beta'^*) - E & & \\ & & & & \alpha + 2\mathcal{R}(\omega^2\beta') - E & \\ & & & & & \alpha + 2\mathcal{R}(\omega^2\beta'^*) - E \end{vmatrix} = 0$$

all off-diagonal elements vanishing. Here (see I) $\beta' = \beta e^{\theta}$ where θ is related to the field strength H and to S , one sixth of the area of a benzene ring†, by $\theta = 2\pi(e/hc)HS$.

We therefore have six distinct energy levels: putting $x = (E - \alpha)/\beta$ and expanding as far as terms in θ^2 we find

$$\begin{aligned}\Gamma_1 \quad x &= 2 - \theta^2 \\ \Gamma_2 \quad x &= -2 + \theta^2 \\ \Gamma_3 \quad x &= 1 - \sqrt{3}\theta - \frac{1}{2}\theta^2 \\ \Gamma_4 \quad x &= 1 + \sqrt{3}\theta - \frac{1}{2}\theta^2 \\ \Gamma_5 \quad x &= -1 - \sqrt{3}\theta + \frac{1}{2}\theta^2 \\ \Gamma_6 \quad x &= -1 + \sqrt{3}\theta + \frac{1}{2}\theta^2\end{aligned}$$

the equations being labelled by the representations to which the associated wave functions belong. The occupied states belong to $\Gamma_1, \Gamma_3, \Gamma_4$, and since the total π -electron susceptibility is proportional to the coefficient of θ^2 summed over the occupied states it follows that, in appropriate units, $\chi_B = -2$.

For comparison purposes it is then sufficient to evaluate Σx_2 for the various molecules from the occupied energy levels, $x = x_0 + x_1\theta + x_2\theta^2$. It will be noticed that those levels which are degenerate in the absence of the field give equal contributions to the susceptibility—in accordance with I, Appendix I.

§ 2. APPLICATION TO CORONENE AND OTHER STRUCTURES

The largest molecule to be considered (Molecule 7, Figure 1) contains 54 carbon atoms whose 2p orbitals $\phi_1, \dots, \phi_{54}$ provide the basis for a representation of dimensionality 54: it is, however, not difficult to pick out a set of functions adapted to a complete decomposition into 54 uni-dimensional representations. For every atom belongs to a group of six equivalent atoms in the molecule (in Figure 2 the 'first' atom in each of the groups, A, B, C, . . . is labelled) and if the 54 required m.o.'s are divided into corresponding sets, based on A-atoms, B-atoms, etc. then the representation will be the direct sum of nine six-dimensional representations: if now the six functions within each set are constructed from the available ϕ 's exactly as in (2), then the representation based on the resulting 54 functions will be completely reduced. Grouping together functions belonging to the same irreducible representation, the secular determinant will be reduced into a product of six determinants of ninth order involving functions $A_r, B_r, \dots, I_r$ where C_r is conveniently used to denote that function belonging to set C and to irreducible representation Γ_r . The typical ninth order determinant is found to be

$$\Delta(x, y) = \begin{vmatrix} -x + 2\mathcal{A}(yk) & 1 & & & & & & & \\ 1 & -x & k^2 & k^{*2} & & & & & \\ & k^{*2} & -x & yk^3 & k^* & & & & \\ & k^2 & y^*k^{*3} & -x & & k & & & \\ & & k & & -x & & k^{*4} & k^3 & \\ & & & k^* & & -x & k^4 & & k^{*3} \\ & & & & k^4 & k^{*4} & -x & & \\ & & & & k^{*3} & & & -x & yk^5 \\ & & & & & k^3 & y^*k^{*5} & -x & \end{vmatrix} \quad (3)$$

† cf. II. S is here re-defined so as to give a numerically simpler secular equation.

where $k = e^{i\theta}$. From (3) six determinants are derived by putting, in turn, $y = 1$, $y = -1$, $y = \omega$, $y = \omega^*$, $y = \omega^2$, $y = \omega^{*2}$. Here the functions are arranged in order $A_1, B_1, \dots, I_1, A_2, B_2, \dots, I_2, \dots$ (see Figure 2) and the corresponding secular determinants for a whole series of molecules may be obtained by deleting various rows and columns.

The structures we shall consider are shown in Figure 1: of these only benzene and coronene are known molecules but, in principle, there appears to be no reason for the non-existence of several of the others. On the other hand structures such

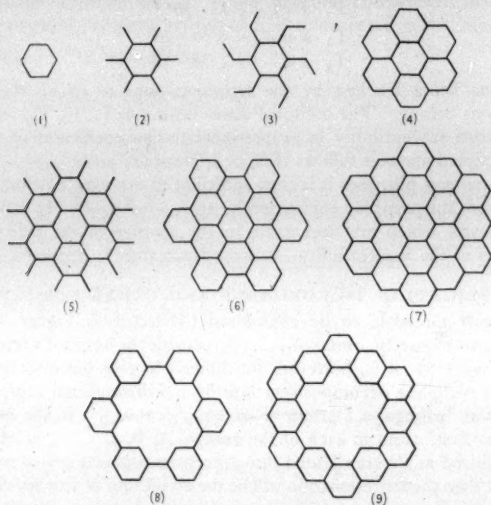


Figure 1. Molecules 1 to 9.

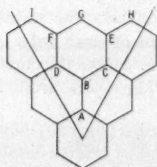


Figure 2. One-sixth of Molecule 7, showing labelling of typical atoms.

as Molecule 2 are admittedly hypothetical. This is, however, of little consequence since it is our purpose at this stage to examine the dependence of magnetic anisotropy on molecular characteristics in general, rather than to effect a detailed comparison of experiment and theory.

Algebraic expansion of the various determinants, up to the ninth order, is not difficult but the subsequent calculation of Σx_2 becomes tedious for the larger molecules and a new technique (see §3) is desirable. Here, however, we shall

illustrate the direct treatment by an application to coronene. This molecule has been considered by Squire (1938)* and has been the subject of some controversy (Squire 1938, Rogers 1947); Squire's calculations, however, contain a number of errors.

(i) Coronene

The secular determinant, derived from (3) by retaining elements in the first four rows and columns only, is easily expanded giving

$$\Delta_4(x, y) = (-x + 2\mathcal{H}(yk))[-x(x^2 - 3) + 2\mathcal{H}(yk^2)] - (x^2 - 1). \dots (4)$$

Putting in turn, $y=1, -1, \omega, \omega^*, \omega^2, \omega^{*2}$, and neglecting terms in $\theta^3, \theta^4, \dots$, this gives the six secular equations

$$\Gamma_1 \Delta_4(x, 1) = (x^4 - 2x^3 - 4x^2 + 4x + 5) + (x^3 + 46x - 100)\theta^2 = 0$$

$$\Gamma_2 \Delta_4(x, -1) = (x^4 + 2x^3 - 4x^2 - 4x + 5) + (-x^3 - 46x - 100)\theta^2 = 0$$

$$\Gamma_3 \Delta_4(x, \omega) = (x^4 - x^3 - 4x^2 + 2x + 2) + \sqrt{3}(x^3 + 4x - 8)\theta + \frac{1}{2}(x^3 + 46x - 8)\theta^2 = 0$$

$$\Gamma_4 \Delta_4(x, \omega^*) = (x^4 - x^3 - 4x^2 + 2x + 2) + \sqrt{3}(-x^3 - 4x - 8)\theta + \frac{1}{2}(-x^3 - 46x - 8)\theta^2 = 0$$

$$\Gamma_5 \Delta_4(x, \omega^2) = (x^4 + x^3 - 4x^2 - 2x + 2) + \sqrt{3}(x^3 + 4x + 8)\theta + \frac{1}{2}(-x^3 - 46x - 8)\theta^2 = 0$$

$$\Gamma_6 \Delta_4(x, \omega^{*2}) = (x^4 + x^3 - 4x^2 - 2x + 2) + \sqrt{3}(-x^3 - 4x + 8)\theta + \frac{1}{2}(x^3 + 46x - 8)\theta^2 = 0.$$

Since the solutions of Γ_3, Γ_4 , and likewise of Γ_5, Γ_6 , yield equal contributions to Σx_2 (I, Appendix I), it is sufficient to consider the four equations $\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_5$. Each equation is of the form

$$\Delta(x, y) = \Delta_0(x, y) + f_1(x, y)\theta + f_2(x, y)\theta^2 = 0 \dots (5)$$

the suffix zero indicating the zero-field secular equation whose roots (x_0) are supposed known. Neglecting terms in $\theta^3, \theta^4, \dots$ approximate solutions of the form $x = x_0 + x_1\theta + x_2\theta^2$ may be found by making Taylor expansions of $\Delta_0(x, y)$, $f_1(x, y)$, $f_2(x, y)$ (taking $x = x_0 + h$ with $h = x_1\theta + x_2\theta^2$) and equating to zero the coefficients of θ and θ^2 in (5).

Calculating the x_2 's in this way for all the occupied energy levels and summing we find, for coronene, $\Sigma x_2 = -19.592$. Consequently $\Delta\chi/\Delta\chi_B = 9.795_5$.

(ii) Other Structures

This method may be applied to each molecule: the results of our calculations are summarized in the Table. So far the non-orthogonality of adjacent atomic orbitals has been neglected but the results are easily modified (Brooks 1941) to admit an overlap integral $\delta = 0.25$ (the value usually assumed): the modified results are also given in the Table.

Molecule	Diamagnetic Anisotropies $\Delta\chi/\Delta\chi_B$								
	1	2	3	4	5	6	7	8	9
No overlap	1.0	0.0405 ₀	0.589 ₈	9.795 ₉	0.771 ₂	14.94 ₈	35.03 ₃	5.266 ₀	17.85 ₅
Overlap=0.25	1.0	0.0293 ₈	0.604 ₉	10.13 ₄	0.827 ₁	15.36 ₁	36.65 ₇	5.307 ₈	17.81 ₀
Pauling theory	1.0	1.0	1.0	13.87	14.57	29.20	68.98	34.86	65.29

* The method of calculation is not fully described.

§ 3. AN ALTERNATIVE TREATMENT OF THE REDUCED SECULAR EQUATIONS

Whilst the above method of calculating Σx_2 by summation of one-electron contributions is quite simple in the case of small molecules, particularly when the unperturbed energy levels are known, it becomes extremely tedious when applied to very large molecules. We shall now show how Σx_2 may be obtained directly by contour integration: in this way the diamagnetic anisotropy may be calculated, *without any knowledge of the energy levels or wave functions of the unperturbed molecule*.

Consider the n th degree secular equation (in general with $\theta \neq 0$) $f(x)=0$, with n real and distinct roots ($x=x', x'', \dots x^{(n)}$). In the m.o. approximation the total energy of n electrons doubly occupying the negative energy levels is (in units β above the zero level $n\alpha$) $2\Sigma x$ where the summation is over the occupied levels and may be obtained from the identity (Coulson 1940)

$$\Sigma x = \frac{1}{2\pi i} \int_C \left\{ \frac{zf'(z)}{f(z)} - n \right\} dz. \quad \dots\dots(6)$$

Here the contour consists of the y axis and an infinite semicircle to the right* of this axis. The inclusion of $-n$ in the integrand conveniently ensures (at least in the case $\theta=0$) the vanishing of the integral over the circular contour. The substitution $z=iy$ then gives

$$\Sigma x = -\frac{1}{2\pi} \int_{-\infty}^{+\infty} \left\{ \frac{iyf'(iy)}{f(iy)} - n \right\} dy. \quad \dots\dots(7)$$

If $f(x)$ is an even function the integrand is real and numerical integration is straightforward; otherwise rationalization is necessary. Now in our case $\Sigma x = \Sigma x_0 + \theta \Sigma x_1 + \theta^2 \Sigma x_2$ and we require Σx_2 only: clearly this quantity may be obtained directly as the integrated coefficient of θ^2 in the expansion of the integrand in powers of θ .

Since our equations are not, individually, even functions of x it would at first seem necessary both to rationalize and to expand in powers of θ , thereby obtaining a very complicated integrand. It appears, however, that our six equations may be paired and the pairs,

$$\begin{pmatrix} \Delta(x, 1) & = 0 \\ \Delta(x, -1) & = 0 \end{pmatrix}, \quad \begin{pmatrix} \Delta(x, \omega) & = 0 \\ \Delta(x, \omega^*) & = 0 \end{pmatrix}, \quad \begin{pmatrix} \Delta(x, \omega^2) & = 0 \\ \Delta(x, \omega^*) & = 0 \end{pmatrix}, \quad \dots\dots(8)$$

may each be written in the form

$$\begin{aligned} \Delta_+ &= \{A_1(x) + A_2(x)\} + \{B_1(x) + B_2(x)\}\theta + \{C_1(x) + C_2(x)\}\theta^2 = 0 \\ \Delta_- &= \{A_1(x) - A_2(x)\} + \{B_1(x) - B_2(x)\}\theta + \{C_1(x) - C_2(x)\}\theta^2 = 0 \end{aligned} \quad \dots\dots(9)$$

where A_1, B_1, C_1 and A_2, B_2, C_2 are respectively odd and even functions of x . If now we take $f(x) = \Delta_+ \Delta_-$ a relatively simple *even* function of x is obtained and the integration outlined above gives the summed coefficients Σx_2 , arising from the roots of *both* Δ_+ and Δ_- . Also, as we have already seen, the last two pairs in (8) must give equal contributions Σx_2 . It remains therefore, to evaluate two infinite integrals for each molecule.

* We require Σx over the *positive* roots since our β is a negative quantity.

We find, on putting

$$A = A_1^2 - A_2^2, \quad B = 2(A_1B_1 - A_2B_2), \quad C = 2(A_1C_1 - A_2C_2) + (B_1^2 - B_2^2),$$

(so that $f(x) = A + B\theta + C\theta^2$)

$$\Sigma x_2 = -\frac{1}{\pi} \int_0^\infty \left\{ \left(\frac{A\bar{C} - \bar{A}C}{A^2} \right) + \left(\frac{A\bar{A}B^2 - B\bar{B}A^2}{A^3} \right) \right\} dy \quad \dots (10)$$

where $\bar{A} = (x\partial A/\partial x)$, $\bar{B} = (x\partial B/\partial x)$, $\bar{C} = (x\partial C/\partial x)$ and $x = iy$ throughout.

In the cases with which we deal the coefficient of θ^2 in the integrand of (6) vanishes at least as strongly as x^{-2} —hence the absence of any contribution from the circular contour. The simple polynomials $A, B, C, \bar{A}, \bar{B}, \bar{C}$, contain up to nine terms in the case of Molecule 7, so the integrand of (10) is best evaluated numerically without further algebraic expansion. It should be noted that the integral associated with the first pair of equations in (8) is relatively simple, the second term in (10) vanishing. Also each of the two integrals required for a given molecule is determined mainly by the region $0 < y < 4$: an asymptotic expression is easily derived for the integral from 4 to ∞ . If the roots x_0 are in the first place unknown the determination of Σx_2 by this method may involve considerably less labour than proceeding by way of the numerical solution of the secular equations.

The Inclusion of Overlap

The contour integral method of obtaining the total π -electron energy can be modified to take overlap into account. The treatment given by de Heer (1950) may be applied directly to magnetic problems, for, with overlap δ and replacement of β by $\gamma = \beta - \delta x$, the modified total energy is found using

$$\Sigma x = -\frac{1}{2\pi} \int_{-\infty}^{+\infty} \frac{1}{1 + \delta^2 y^2} \left\{ \frac{iyf'(iy)}{f(iy)} - n \right\} dy \quad \dots (7')$$

instead of (7). Now in obtaining Σx_2 with neglect of overlap, we have simply expanded the quantity in brackets in powers of θ and selected the θ^2 term as a measure of the π -electron susceptibility; since the factor $(1 + \delta^2 y^2)^{-1}$, introducing the overlap correction, is common to every term in the expansion, it is clear that the modified Σx_2 may be calculated directly from (10) provided the integrand is weighted with the factor $(1 + \delta^2 y^2)^{-1}$. The smallness of δ^2 suggests immediately that overlap should have little effect on our calculations; it appears moreover, as de Heer has shown for the total energies, that the modification is roughly equivalent to multiplication by a factor which differs little from molecule to molecule. The ratio $\Delta\chi/\Delta\chi_B$ might therefore be expected to show very little dependence on overlap.

This result is a quite general one provided we use simple m.o. theory and deal only with pure hydrocarbons; it therefore explains immediately previous observations that the calculated anisotropy is not strongly dependent on overlap (II, Brooks 1941). Whenever the secular determinant, involving a perturbation parameter of any kind, can be made formally similar to that obtaining without overlap by the change of variables $x \rightarrow x/(1 + \delta x)$, $\beta \rightarrow \beta - \delta x$ then the total perturbation energy, in any order, is only weakly dependent on overlap. The conditions under which this reduction is possible have been examined by Chirgwin and Coulson (1950); it is important to notice that a similar result cannot be established for molecules containing hetero-atoms.

§4. DISCUSSION

In the Table our results are accompanied by the values of $\Delta\chi/\Delta\chi_B$ calculated using the semi-classical method of Pauling (1936). Both types of calculation predict a steady rise of $\Delta\chi/\Delta\chi_B$ for Molecules 1, 4, 6, 7, although quantitatively there is considerable divergence; but startling contradictions appear elsewhere. It is evident that the Pauling method is, in general, likely to be misleading: in seeking an explanation we shall examine separately the different kinds of molecule.

Molecules 1, 4, 6, 7

The only structures considered hitherto have been of this type* (II, London 1937); they are completely condensed cyclic hydrocarbons in which every carbon atom is included in at least one six-membered ring and there are no 'holes' in the structure (cf. Molecules 8, 9). Although for the smaller molecules considered in these papers and elsewhere (up to, say, coronene) the Pauling theory has shown itself of value as a crude substitute for the more complete theory, our results show clearly that, even in the most favourable circumstances, it must be abandoned in dealing with very large molecules. On the other hand the results of m.o. theory appear to be entirely plausible and our contention that the computed values of $\Delta\chi/\Delta\chi_B$ should be more or less independent of overlap is well substantiated. Indeed, this near-independence is observed with every molecule considered, with one exception: for Molecule 2 the integral (7') has an abnormally low value, arising from cancellation of negative and positive areas—in this case the whole integral is not insensitive to changes in δ .

Molecules 2, 3, 5

The Pauling treatment is evidently quite inapplicable even to small molecules when these possess 'stray' C-C bonds (i.e. bonds not contained in a ring). It is, however, still desirable to seek some physical interpretation of our results.

The sudden drop in susceptibility in going from Molecule 1 to Molecule 2 would be explicable immediately if there were considerable 'bond fixation' but calculations of resonance energy and bond order preclude this possibility: in the language of valence-bond theory this means that, even in the ground state, the single 'fixed-bond' structure (all stray bonds double) must be supplemented by important excited structures. The extremely small π -electron susceptibility cannot therefore be attributed to bond fixation, but the very fact that the only possible unexcited structures show the stray bonds double also places a restriction upon the *types* of excited structures which can be drawn; and the existence of an appreciable susceptibility is linked with the occurrence of certain *particular* types. Thus Brooks (1940) has shown that an appreciable susceptibility can occur only when there exists a group of excited structures by means of which an electron can be 'passed round the ring'.

Now in the case in point there are clearly no structures of this type, for no ring-atom can possess an unbonded electron in any valence bond structure; if the atom is not shown bonded to either of its neighbours in the ring it must be bonded to the adjacent stray carbon atom which can always provide an electron for such a bond. It should be noticed that excited states showing unbonded those atoms *not* contained in the ring do not contribute very much to the susceptibility because (see Brooks 1940) the relevant resonance integrals then involve non-adjacent atoms. The extremely small value of $\Delta\chi/\Delta\chi_B$ predicted for Molecule 2 by m.o. theory thus finds support in qualitative valence bond

* With one exception: Evans, de Heer and Gergely (1949).

considerations: this is a very pleasing result in view of the impossibility of dealing with the vast numbers of valence bond structures involved in the larger molecules.

This interpretation also explains a similar effect noted by other writers (Evans, de Heer and Gergely 1949) in an application of m.o. theory to p-benzoquinodimethane: in this case there are two carbon atoms within the benzene ring which cannot show free electrons in any valence-bond structure and therefore serve as 'barriers' tending to prevent the passage of electrons round the ring.

Passing now to Molecule 3, it is evident that structures in which the peripheral atoms are bonded are no longer incompatible with the presence of free electrons on ring-atoms; indeed, if structures of this kind only were involved we should expect the system to show little difference, magnetically, from the simple benzene ring. The considerable rise in $\Delta\chi/\Delta\chi_B$ is thus to be anticipated.

The addition of stray carbon atoms to coronene might be expected to annul the effectiveness of the outermost complete ring of carbon atoms, exactly as in the case of Molecule 2, so that $\Delta\chi$ for Molecule 5 should have a value only of the order $\Delta\chi_B$. Our results support this conclusion and it seems likely that the effect is quite a general one: bordering a condensed structure with stray carbon atoms reduces the magnetically effective size of the system.

The above results may be significant in discussing the effect of different kinds of 'edge' upon the magnetic properties of carbon particles. Taking as a 'standard edge' that in which the free carbon valencies are satisfied by hydrogen atoms, we suggest that (i) replacement of hydrogens, $-H$, by $-C\begin{smallmatrix} H \\ H \end{smallmatrix}$ leads to a marked reduction in the magnetically effective size of a carbon particle, roughly equivalent to striking out all those rings with one or more such groups attached (cf. Molecules 2, 5); (ii) replacement of hydrogens, $-H$, by 'actylenic tails', $-C\equiv CH$, has little effect on the susceptibility of the original particle. This is suggested by the fact that the secular determinant for such a system, e.g. benzene with six 'tails', is formally identical with that for a system of a type already considered, Molecule 2.

Molecules 8, 9

The removal of atoms from the centre of a condensed system evidently has a very marked effect on $\Delta\chi/\Delta\chi_B$; moreover, the effect may be entirely the opposite of that predicted on semi-classical grounds*. Thus, on Pauling's theory, the magnetic anisotropy of 'ring molecules' such as 8 and 9 should depend jointly on the area of the whole ring (roughly that of the molecule) and on the 'conductivity' of the ring, the latter presumably being larger for Molecule 9 than for Molecule 8 because of the increased number of 'conducting' bonds. The reason for the failure of this theory is primarily the assumption of *independent* ring currents; the necessary interdependence of these currents is easily illustrated by valence bond considerations.

Unfortunately a thorough valence bond treatment of Molecules 8 and 9 is precluded by the vast number of available structures; we shall merely make the customary assumption that in general the higher the order of an excited structure the less its contribution to the ground state wave function. Consider now Molecule 8: by far the most abundant of the less highly excited structures are those in which two opposing atoms in each ring possess unpaired electrons. This

* On Pauling's theory the susceptibility/carbon atom for Molecule 9 is not *less* than that for Molecule 7 but *greater*.

group of structures makes it possible for electrons to 'hop' round the individual benzene rings, but it cannot give a net flow *between* the rings. In classical language the two conducting paths (inner and outer) which encircle the whole molecule must carry equal and opposite currents: on the other hand the Pauling theory predicts a large current along each path *in the same direction*. If only the excited structures above were involved in the ground state wave function we might therefore expect a value of $\Delta\chi/\Delta\chi_B$ of the order 6.0, corresponding to that for six unconnected benzene rings. Actually other structures, in which the connecting bonds are shown double, must be involved if there is appreciable conjugation between the rings, but it is not difficult to see that these also cannot be responsible for electron-hopping around the entire periphery of the molecule, and their presence therefore serves only to reduce the weight of those structures giving benzene-type ring currents. The value $\Delta\chi/\Delta\chi_B = 5.3$, given in the Table conforms quite well with these conclusions.

In Molecule 9 the restrictions on the types of excited structure possible are considerably less severe: there is now a much greater variety of possible electron-hopping paths encircling more than one benzene ring. We may therefore expect $\Delta\chi$ to be considerably greater than for twelve independent rings although less than that for the whole molecule (7) in which the restrictions are even further relaxed. The value $\Delta\chi/\Delta\chi_B = 17.8$ thus appears quite plausible, whereas the semi-classical result (65.3) even fails to suggest the marked difference between Molecules 7 and 9.

ACKNOWLEDGMENTS

The author's thanks are due to Professor C. A. Coulson for very kindly providing numerical values of some of the energy levels (α_0) used in this paper. He is also indebted to his wife for assistance with the calculations.

APPENDIX

Parts I and II. Errata

Several errors had arisen in I and II (McWeeny 1951) during preparation of the MSS. They are:

The exponent should be reversed in sign in equation (4), p. 265 and in line 9, p. 267; it should be halved in equation (6), p. 265: it should be halved and reversed in sign in line 8, p. 267.

Last line, p. 274, should read: $U = -\frac{1}{2}HYx' + \frac{1}{2}HXY' = \frac{1}{2}\mathbf{R} \cdot \mathbf{r}' \times \mathbf{H} = -\mathbf{R} \cdot \mathbf{A}'$, and in line 4, p. 275, $\exp\{-2\pi i \mathbf{x} \cdot \mathbf{A}\}$ should read $\exp\{2\pi i \mathbf{x} \cdot \mathbf{A}'\}$.

REFERENCES

- BROOKS, H., 1940, *J. Chem. Phys.*, **8**, 939; 1941, *Ibid.*, **9**, 463.
 CHIRGWIN, B. H., and COULSON, C. A., 1950, *Proc. Roy. Soc. A*, **201**, 196.
 COULSON, C. A., 1940, *Proc. Camb. Phil. Soc.*, **36**, 201.
 EVANS, M. G., DE HEER, J., and GERGELY, J., 1949, *Proc. Phys. Soc. A*, **62**, 505.
 DE HEER, J., 1950, *Phil. Mag.*, **41**, 370.
 LONDON, F., 1937, *J. Phys. Radium*, **8**, 397.
 MCWEENY, R., 1951, *Proc. Phys. Soc. A*, **64**, 261.
 PAULING, L., 1936, *J. Chem. Phys.*, **4**, 673.
 ROGERS, M. T., 1947, *J. Amer. Chem. Soc.*, **69**, 1506.
 SQUIRE, C. F., 1938, *C.R. Acad. Sci., Paris*, **206**, 665.

LETTERS TO THE EDITOR

Paramagnetism of Cerium Ethylsulphate at Low Temperatures

Single crystals of cerium ethylsulphate, $\text{Ce}(\text{C}_2\text{H}_5\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}$, have been investigated at liquid helium temperatures by measurements of susceptibility and by paramagnetic resonance experiments. This substance shows no paramagnetic resonance at temperatures above 20°K ., the spin-lattice relaxation time being so short that the absorption lines are broadened to such an extent as to be undetectable (Bleaney and Scovil 1951). According to the theory of Elliott and Stevens (unpublished) the $^2F_{5/2}$ ground state of cerium ion is split by the crystalline field in this salt into three doublets with $J_g = \pm 1/2, \pm 3/2, \pm 5/2$, the z axis being the hexagonal axis of symmetry of the crystal. The $\pm 3/2$ level is some 130 cm^{-1} above the others, so that its population is negligible at temperatures below 20°K . Our experiments have enabled us to find the magnetic properties and energy separation of the other two levels.

The resonance experiments were made in the usual way, the absorption in the specimen being measured by its effect on the damping of a cavity resonator and displayed on a cathode-ray tube as a function of the applied magnetic field. The resonant wavelength was 3.25 cm . Experiments were made on a dilute salt (a mixed crystal of one part cerium ethylsulphate and 200 parts of lanthanum ethylsulphate) and on a concentrated salt. The liquid helium used was obtained from a large Simon expansion liquefier with transfer siphon, which has just been brought into use in this laboratory.

At 4.2°K two resonance lines were found in the diluted salt, one due to the $\pm 5/2$ level and the other to the $\pm 1/2$ level. The results may be expressed in terms of the following spectroscopic splitting factors, or g -values (defined by $h\nu = g\beta H$, where h = Planck's constant, β = Bohr magneton, ν = resonant frequency in a magnetic field H); $g_{\parallel}$ and $g_{\perp}$ are the g -values in a magnetic field respectively parallel and perpendicular to the crystal axis:

$$g_{\parallel}(5/2) = 3.70 \pm 0.02, \quad g_{\perp}(5/2) = 0.35 \pm 0.15, \quad g_{\parallel}(1/2) = 1.02 \pm 0.02, \quad g_{\perp}(1/2) = 2.17 \pm 0.02.$$

At an angle θ to the axis the g -value is given by $g^2 = g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta$.

At 4.2°K the $J_g = \pm 1/2$ line was about ten times as intense as the $J_g = \pm 5/2$ line, both measured near the angle at which their g -values are equal. From the change in their relative intensities as the temperature was lowered to 2.5°K it is concluded that the $\pm 1/2$ level lies lower by $3 \pm 1 \text{ cm}^{-1}$. An interesting feature of the results is that in this salt we are able to observe absorption due to an excited state. Moreover, this absorption arises from a transition in which $\Delta J_g = 5$.

In the concentrated salt no resonance was detected at 4.2°K except for a line from neodymium present as an impurity. The width of this line was markedly dependent on the orientation of the crystal, being narrowest with the magnetic field perpendicular to the crystal axis, and three times broader at 15° to this direction. In accordance with recent work by Bleaney, Elliott and Scovil (1951), the broadening of the neodymium line is proportional to the g -value of the broadening agent, which is therefore cerium in the $\pm 5/2$ state. On cooling to 2.5°K a very broad line (line width approximately 700 gauss) appeared with g -values depending on angle in a similar way to that of the $\pm 5/2$ state in the dilute salt. It is concluded that in the concentrated salt the $\pm 5/2$ state lies lowest, contrary to the case of the dilute salt.

This conclusion is confirmed by the susceptibility measurements, which were made on four single crystals mounted together with their hexagonal axes parallel. Measurements were made with this axis (a) parallel and (b) perpendicular to the measuring field, using the apparatus and method described elsewhere (Benzie and Cooke 1950). Only the temperature-dependent paramagnetism is measured. The results indicate that in the temperature range 1°K to 20°K there are two levels contributing to the susceptibility,

and that the $\pm 5/2$ level is the lower. In terms of g -values the susceptibility χ of such a system should be, to a first approximation,

$$\chi = \frac{N\beta^2}{4kT} \frac{g_{5/2}^2 + g_{1/2}^2 e^{-\Delta/T}}{1 + e^{-\Delta/T}}$$

where $\hbar\Delta$ is the energy separation of the two states. Good agreement with experiment is found by taking $g_{5/2}(5/2) = 3.80 \pm 0.04$, $g_{1/2}(5/2) = 0 \pm 0.4$, $g_{5/2}(1/2) = 1.0 \pm 0.2$, $g_{1/2}(1/2) = 2.25 \pm 0.2$, and $\Delta = 7.5^\circ \pm 1.5^\circ \text{ K}$.

Previous measurements of the susceptibility have been made at temperatures down to 14° K . by Fereday and Wiersma (1935) and to temperatures down to 1.37° K , in the parallel direction only, by Becquerel *et al.* (1938), who used the Faraday effect and assumed that the rotation of polarized light was proportional to the susceptibility, as verified by measurements above 14° K . The results of Becquerel *et al.* in the parallel direction are in good agreement with ours. In order to fit the results of Fereday and Wiersma in the perpendicular direction a temperature-independent term must be added. This would be measured in their experiments but not in ours. The presence of such a term may be accounted for theoretically (Van Vleck 1928); it is due to off-diagonal elements in the magnetic moment matrix connecting the $J_z = \pm 3/2$ state with the ground states.

The final expressions for the susceptibility in E.M.U. per gm.mole, valid up to 20° K , are:

$$\chi_{\parallel} = \frac{0.094}{T} \frac{14.44 + e^{-7.5/T}}{1 + e^{-7.5/T}}, \quad \chi_{\perp} = \frac{0.094}{T} \frac{5.0e^{-7.5/T}}{1 + e^{-7.5/T}} + 4.7 \times 10^{-4}.$$

At higher temperatures the effect of the $J_z = \pm 3/2$ level must be taken into account, and results at 60° K . already lie off the curve.

The results show that this substance is of particular interest for experiments below 1° K . by the adiabatic demagnetization method. At such temperatures only the $\pm 5/2$ state is occupied, and our results show that the susceptibility is at least a hundred times greater along the crystal axis than at right angles to it. We propose, therefore, to make experiments by magnetizing a single crystal in a large magnetic field at 1° K ., and then to cool it by adiabatic demagnetization. The magnetic axis of the crystal, the magnetic field used for cooling, and the coils used for measuring the susceptibility will all be parallel (vertical). After such a demagnetization a horizontal magnetic field may be applied without much effect on the temperature of the specimen. In effect the specimen has been cooled by rotation of the magnetic field. Cerium ethylsulphate is therefore of value for cooling substances on which it is desired to make magnetic experiments at temperatures below 1° K ., for example the investigation of the phase diagram of a superconductor, or nuclear resonance experiments.

We wish to thank Mr. H. E. D. Scovil for supplying the crystals and much helpful advice; also Mr. A. J. Croft and Mr. G. R. Hercus, who provided the liquid helium.

The Clarendon Laboratory,
Oxford.
25th June 1951.

G. S. BOGLE.
A. H. COOKE.
S. WHITLEY.

- BECKEREL, J., DE HAAS, W. J., and VAN DEN HANDEL, J., 1938, *Physica*, **5**, 857.
BENZIE, R. J., and COOKE, A. H., 1950, *Proc. Phys. Soc. A*, **63**, 201.
BLEANEY, B., ELLIOTT, R. J., and SCOVIL, H. E. D., 1951, *Proc. Phys. Soc. A*, **64**, in the press.
BLEANEY, B., and SCOVIL, H. E. D., 1951, *Proc. Phys. Soc. A*, **64**, 204.
FEREDAY, R. A., and WIERSMA, E. C., 1935, *Physica*, **2**, 575.
VAN VLECK, J. H., 1928, *Phys. Rev.*, **31**, 587.

The Paramagnetism of Cerium Ethylsulphate: Theory

The theory of the resonance phenomena in rare earth ethylsulphates as reported in a previous letter (Elliott and Stevens 1951) has now been taken to second order in perturbation theory and applied to cerium ethylsulphate. The experimental results on this salt have been reported by Bogle, Cooke and Whitley (1951) who have obtained accurate g -values, particularly for the dilute salt. We find that their results can be explained

by using the following values for the crystal field parameters, as defined in our earlier letter : $-|e|A_6^0\bar{r}^2=0$, $-|e|A_4^0\bar{r}^4=-70\text{ cm}^{-1}$, $-|e|A_6^4\bar{r}^4=8\text{ cm}^{-1}$, $-|e|A_4^4\bar{r}^4=-130\text{ cm}^{-1}$, $-|e|A_6^6\bar{r}^6=1300\text{ cm}^{-1}$. The crystalline potential used is slightly different from that given previously in that we have included a term of the form $A_4^3z(x^2-3xy^2)$ to account for departures from D_{3h} symmetry. As can be seen from the value given above, this extra term is small, but it proves to have an important effect in this salt because it so happens that the levels corresponding to $J_z=\pm\frac{1}{2}$ and $J_z=\pm\frac{5}{2}$ are near together and a term of this type has matrix elements coupling the two levels. The second order calculation has been made by assuming that only the important contributions come from the other multiplet ($J=7/2$) which we have taken to be 2500 cm^{-1} above the ground multiplet. In the following Table we compare the experimental and theoretical results.

J_z (approx.)	Theoretical g		Experimental g		Theor. energy	Exp. energy
	$g_{ }$	$g_{\perp}$	$g_{ }$	$g_{\perp}$	(cm^{-1})	(cm^{-1})
$\pm\frac{1}{2}$	1.02	2.17	1.02 ± 0.02	2.17 ± 0.02	0	0
$\pm\frac{3}{2}$	3.70	0.42	3.70 ± 0.02	0.35 ± 0.15	3	3 ± 1
$\pm\frac{5}{2}$	2.5	0	—	—	160	—

The values of the parameters are in reasonable agreement with those obtained from a model of the ion and its surroundings but they cannot be regarded as known with any great certainty as it is possible to use appreciably different values and still remain within the experimental errors. If the value of $g_{\perp}$ ($\pm 5/2$) or the properties of the $\pm 3/2$ level were accurately known the crystal field values could also be more closely determined.

In the concentrated salt the uncertainties in the g -values are much greater and there is an even wider range of possible values for the field parameters. Thus at present there is little to be gained by applying the theory in detail to the concentrated salt.

A full account of this work is being prepared and will be published shortly.

Clarendon Laboratory,
Oxford.
4th July 1951.

R. J. ELLIOTT.
K. W. H. STEVENS.

BOGLE, G. S., COOKE, A. H., and WHITLEY, S., 1951, *Proc. Phys. Soc. A*, **64**, 931.
ELLIOTT, R. J., and STEVENS, K. W. H., 1951, *Proc. Phys. Soc. A*, **64**, 205.

Dipole-Dipole Interaction in the Rare-Earth Ethylsulphates

Paramagnetic resonance spectra of several rare earth ethylsulphates show interesting features in line shape which can be related to spin-spin and spin-lattice effects in the crystal. The former gives usually a broadening of the resonance lines which is due to the magnetic fields in neighbouring ions, randomly superimposed. This broadening consists really of a closely spaced fine structure, some detail of which can be resolved if the crystal is diluted with an isomorphous diamagnetic salt (Bleaney and Ingram 1950). The ethylsulphates are, however, sufficiently dilute themselves to give some resolution.

The spectrum of neodymium ethylsulphate at 20°K . is shown in Figure 1. With the magnetic field parallel to the hexagonal axis a triplet structure is visible; this is not due to hyperfine structure, which gives lines of only $1\frac{1}{2}\%$ relative intensity. It is well accounted for by dipole-dipole interaction with the next neodymium ions, which lie at a distance $c=7\text{A}$. away along the hexagonal axis. A simple classical picture shows that the resultant field of these two neighbours is $\pm 2g_{||}\beta/c^3$, or 0, the latter being twice as probable as either of the former. Thus we expect a triplet line, with a spacing of about $50g_{||}=180$ gauss, the satellites having half the intensity of the centre line. The rotating fields of the neighbours give a resonance interaction which is small owing to the low value of $g_{\perp}$; this should slightly increase the splitting. With a field perpendicular to the axis, the classical splitting should be $25g_{\perp}=50$ gauss and the resonance displacement is more important; the triplet is not resolved though the shape indicates the presence of the satellite lines. Broadening by the

more distant neighbours gives a root mean square width (Van Vleck 1948, Pryce and Stevens 1950) of approximately 45 gauss for either direction, which is consistent with experiment.

The resonance in a concentrated gadolinium ethylsulphate crystal was observed as a wide line some thousands of gauss broad. The elementary picture here is complicated by the fact that the neighbouring gadolinium ions are now dipoles with eight possible orientations instead of two. Thus the nearest neighbours alone will give a large number of lines stretching out to $\pm 14 g \beta / c^3 = \pm 700$ gauss from the centre of each line of the gadolinium fine structure. The seven lines of the latter are therefore spread out into one broad line.

The effect of spin-spin broadening on the spectrum of an impurity was observed in a crystal of neodymium ethylsulphate containing about 0.2% of the gadolinium salt. At 90° K. the neodymium spectrum is invisible owing to the very short spin-lattice relaxation time, and for the same reason the Gd spectrum (Figure 2 top) shows only the width normal for high dilution; this width is due to the nuclear moments of the protons in the water of crystallization. At 20° K. the relaxation time of Nd is so long ($> 10^{-8}$ seconds) that the full effect of its dipole field is observed in the Gd spectrum (Figure 2 centre), each line being split into three. With dissimilar ions there are no resonance effects and the classical picture is a better approximation than in the concentrated Nd salt. Thus the intervals

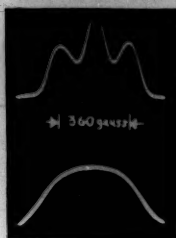


Figure 1. Triplet structure of the neodymium line in neodymium ethylsulphate: Top, magnetic field parallel to crystal axis; bottom, magnetic field perpendicular to axis.

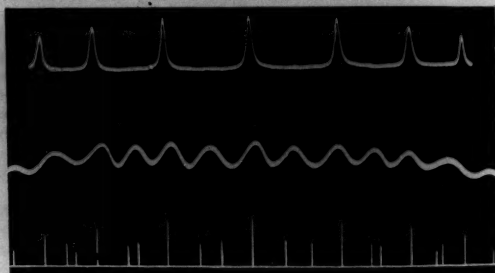


Figure 2. Gadolinium impurity spectrum in neodymium ethylsulphate. Top, at 90° K.; centre, at 20° K.; bottom, theoretical spectrum at 20° K.

of the triplet should be 180 gauss when the spectrum is observed parallel to the axis. As the fine structure intervals in Gd are about 300 gauss, some of the satellite lines overlap so that 13 lines are observed in all. The root mean square width should be about 40 gauss which is of the order observed experimentally.

Similar experiments have been made with gadolinium impurity in cerium and samarium. No transitions due to either of these two ions have been observed down to 14° K. in the ethylsulphates. In the samarium salt the Gd impurity spectrum appeared to have the normal line width, but in the cerium salt a small broadening of the lines parallel to the axis was visible at 20° K., which increased considerably on pumping down to 14° K. At the same time saturation effects, which are usually present in gadolinium at these temperatures, could not be obtained.

The absence of magnetic resonance lines due to cerium and samarium can be accounted for in two ways: (a) there may be no allowed transitions in the Kramers doublets occupied at these temperatures (this occurs when one of the principal values of the g -tensor is zero); (b) the relaxation time may be so short that the lines are too broad and too weak to detect. In the former case the gadolinium impurity lines should be broadened in directions where the g -values of the Kramers doublets of the predominant ion are not zero. In the latter case no broadening will be observed until the temperature is lowered so far that the relaxation time of the predominant ion approaches the Larmor precession period of the Gd.

The results indicate that (b) is the correct explanation for both samarium and cerium. The absence of saturation effects is due to the shortening of the relaxation time of the Gd impurity through transitions induced by the fluctuating magnetic fields of the rapidly relaxing cerium and samarium ions. In the case of cerium the correctness of this explanation has been confirmed by Bogle, Cooke and Whitley (1951), who found paramagnetic resonance lines at helium temperatures.

Clarendon Laboratory,
Oxford.
4th July 1951.

B. BLEANEY.
R. J. ELLIOTT.
H. E. D. SCOVIL.

BLEANEY, B., and INGRAM, D. J. E., 1950, *Proc. Phys. Soc. A*, **63**, 408.
BOGLE, G. S., COOKE, A. H., and WHITLEY, S., 1951, *Proc. Phys. Soc. A*, **64**, 931.
PRYCE, M. H. L., and STEVENS, K. W. H., 1950, *Proc. Phys. Soc. A*, **63**, 36.
VAN VLECK, J. H., 1948, *Phys. Rev.*, **74**, 1168.

A Geiger Counter Spectrometer for Soft X-Rays

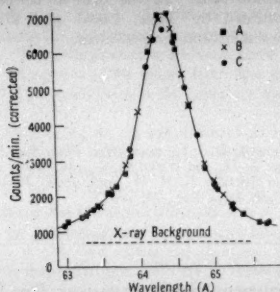
The spectroscopy of soft x-rays, of wavelengths which may be as great as several hundred Angström units, has been made possible by the use of ruled gratings in grazing incidence settings. The x-rays are detected photographically. Wavelengths can be determined with precision, but intensity measurements are of more doubtful accuracy. They usually involve the assumption that the reciprocity law is valid and that the output of the x-ray tube is constant. Chalklin (1948) has used a method which avoided these assumptions, but the uncertainty of the photographic photometry was considerable. Yet intensity measurements are needed to give the precise shapes of the soft x-ray bands that involve the valence electrons and which have afforded striking evidence on the electron theory of solids; and intensity measurements are needed in the study of the absorption of soft x-rays by gases and solids. We have therefore attempted to construct an instrument which, with the photographic plate replaced by a Geiger counter, would make direct measurements of intensity without sacrificing resolution. The purpose of the present Letter is to indicate that this attempt has eventually proved successful. In undertaking the task we were encouraged by the success of the early unfocused counter spectrometers of Neufeldt (1931) and Messner (1933).

Owing to the high absorptivity of the soft x-rays the spectrometer is enclosed in a vacuum box. The optical system consists of a fine slit as effective source, a one-metre Siegbahn concave grating and a 'detector' slit, all mounted on the circle of focus of the grating. The grazing angle of incidence is 2.5° . The detector slit, with the Geiger counter mounted behind it, is moved along the circle of focus, and its position measured, by operations conducted outside the vacuum box. To permit the entry of the soft x-rays the counter is provided with a very thin window consisting of a double celluloid film of total thickness 1,000 Å.

Tests on the Geiger counter with gamma-rays show that, although the counting rate is proportional to the intensity for rates below 3,000 per minute, there is an increasing deviation for higher speeds of counting. Allowance for this has been made in the curve of the Figure, which represents the first order of the molybdenum line $M_{IV,V-N_{II,III}}$. The three sets of points in the Figure correspond to different radiation intensities, and for comparison the B set have been multiplied by 1.12 and the C set by 0.565. The wavelength scale has been obtained from the dispersion curve, and by matching the wavelength of symmetry of each set to the value of 64.35 Å. given by Siegbahn and Magnusson (1934). The agreement of the three sets (if we except the single point at the highest counting rate of 10,000 counts per minute) indicates that the counting rate, when corrected, does indeed measure intensity. The smoothness of the curve indicates the reproducibility and steadiness of the apparatus.

For the instrument to be fully successful it is necessary that the counting rate be great enough to allow accurate readings to be taken at reasonable speed when the slits

are sufficiently narrow to yield satisfactory resolution. The slit widths at present in use yield a theoretical resolving power of roughly 4λ (where λ is the wavelength in Å.), and, with this resolution, it is seen from the Figure that the counting rate is more than adequate



Intensity curve for the first order of the MIV, v-Nu, III line of molybdenum (uncorrected for instrumental line width).

for emission line measurements. Since the highest x-ray tube current was 1 ma., it is clear that it could be increased sufficiently to permit satisfactory measurements to be made of the continuous radiation. Hence it appears that the apparatus should be of value for absorption as well as for emission spectroscopy.

Physics Department,
Canterbury University College,
Christchurch, New Zealand.
29th June 1951.

J. L. ROGERS.
F. C. CHALKLIN.

- CHALKLIN, F. C., 1948, *Proc. Roy. Soc. A*, **194**, 42.
MESSNER, R. H., 1933, *Z. Phys.*, **85**, 727.
NEUFELDT, H., 1931, *Z. Phys.*, **68**, 659.
SIEGBAHN, M., and MAGNUSSON, T., 1934, *Z. Phys.*, **88**, 559.

On the Oscillator Strength of the $x^2\Pi - A^2\Delta$ Transition of the CH Radicle

Stephenson (1951) has recently employed the l.c.a.o. method in calculations on the CH, $x^2\Pi - A^2\Delta$ transition. He finds that the oscillator strength f is about 0.008 and states that this seems to indicate that the value 0.06 assumed by Dunham (1941) is too high and that (considering the nature of the approximation) it is in good agreement with the value 0.002, given both by the experimental work of Lyddane, Rogers and Roach (1941) (as corrected by Dwyer and Oldenberg (1944)) and by the independent theoretical work of Herzberg (quoted by Stromgren (1948)). Astrophysicists eagerly await a reliable determination of the quantity in question. They may, unfortunately, be led into thinking that new evidence has been provided, and that several different approaches now favour the view that f is low as opposed to only a suggestion that it is moderate. Quite apart from the fact that 0.008 is not significantly less than the geometric mean of 0.06 and 0.002, and from the fact that simple calculations on perpendicular-type transitions should be treated with special reserve, it must be pointed out that the summary of the literature which is given is misleading.

(i) The value 0.06 is not based on a mere assumption, it is based on measurements performed by Dunham (1941) in collaboration with King and, moreover, is in concord with an

admittedly indirect deduction made by Gaydon and Wolfhard (1949) from a spectroscopic study of the low-pressure flames.

(ii) Lyddane, Rogers and Roach (1941) did no experimental work; like Stephenson, they used quantum mechanics. They, however, studied a number of transitions and, being doubtful (as well they might be) of the accuracy of the usual approximation to molecular wave functions, they attempted to improve their results by arbitrarily multiplying them by a correction factor which was chosen so as to bring the computed oscillator strength of OH, $x^2\Pi - A^2\Sigma^+$ down to the value obtained in the laboratory by Oldenberg and Rieke (1938). When the latter value was later revised by Dwyer and Oldenberg (1944) it was Herzberg (1950) who made the necessary alteration to the original correction factor and hence estimated f for CH, $x^2\Pi - A^2\Delta$ to be 0.002; he did not carry out a theoretical investigation. There is thus only a single determination, and it is but semi-empirical.

The present letter seeks merely to prevent the growth of any misconception amongst astrophysicists as to the reliability of our knowledge of the oscillator strength of a transition of such importance. It must not be inferred that the writer favours a moderate value; on the contrary he favours a low value.

Department of Applied Mathematics,
Queen's University, Belfast.
8th August 1951.

D. R. BATES.

- DUNHAM, T., 1941, *Publ. Amer. Astr. Soc.* **10**, 123.
 DWYER, R. J., and OLDENBERG, O., 1944, *J. Chem. Phys.*, **12**, 351.
 GAYDON, A. G., and WOLFHARD, H. G., 1949, *Proc. Roy. Soc. A*, **199**, 89.
 HERZBERG, G., 1950, *Spectra of Diatomic Molecules*, 2nd edition (New York: Van Nostrand), p. 386.
 LYDDANE, R. H., ROGERS, F. T., and ROACH, F. E., 1941, *Phys. Rev.*, **60**, 281.
 OLDENBERG, O., and RIEKE, F. F., 1938, *J. Chem. Phys.*, **6**, 439, 779.
 STEPHENSON, G., 1951, *Proc. Phys. Soc. A*, **64**, 666.
 STROMGREN, B., 1948, *Astrophys. J.*, **108**, 242.

On Certain Applications of the Fermi-Thomas Model to the Nucleus

Recent publications (Yang 1951, Ivanenko and Rodichev 1951) on the so-called 'magic numbers' of nuclei (Haxel *et al.* 1949) prompt the following remarks:

- (i) The Fermi-Thomas model by its very nature cannot explain shell formation in its energetic aspect.
- (ii) The other main aspect of shell theory is the prediction of nuclear spins. We may take as basic assumption that the total angular momentum J of an even-odd nucleus is the total angular momentum j of the odd nucleon. This assumption does not necessitate $j-j$ coupling, and the Fermi-Thomas model, which, of course, deals with orbital angular momenta only, is at any rate not inadmissible on these grounds.
- (iii) If we assume a certain nucleonic density distribution (as, for instance, does Yang (1951)) the Fermi model yields the number of nucleons of a given orbital angular momentum, in an approximation which is the W.K.B. approximation to the individual particle solution for the corresponding potential. Further, it shares with the latter all the faults of any individual particle model and, in addition, requires a translation from the continuous to quantized angular momenta which is arbitrary within certain limits.
- (iv) The number n_l of nucleons of a given orbital angular momentum l amounts to one in the statistical model for a total number of nucleons N_1 which is not, in general, at all the same as $N_0 + 1$, where N_0 is the total number of nucleons corresponding to n being exactly zero (e.g. in the case of uniform spatial density the values are $N_1 = 21.1$ as compared with $N_0 = 16.6$ for $l = 3$).
- (v) The first appearance of certain total spins does not coincide with the higher magic numbers; on the shell theory (Mayer 1949) we expect $l = 1, 2, 3, 4$ first to occur for a proton

or neutron number of 3, 9, 21, 41. Using the shell interpretation, we find these l values empirically first in those regions.

(vi) For uniform density the Fermi model determines the absolute values n_l by the equation

$$n_l = [8\{l(l+1)\}^{1/2}/\pi][\{y^2 - l(l+1)\}^{1/2} - \{l(l+1)\}^{1/2} \cos^{-1}[\{l(l+1)\}^{1/2}/y]],$$

where $y = (9\pi N/8)^{1/3}$, N being the total number of nucleons, with no further adjustable or empirical parameter.

The atomic numbers corresponding to first appearance of successive orbital angular momenta calculated from this equation (i.e. for a 'square distribution' of nucleonic density) are too small by a factor of nearly two.

Department of Mathematical Physics,
University of Birmingham.
2nd August 1951.

H. R. PANETH.

HAXEL, O., JENSEN, J. H. D., and SUESS, H. E., 1949, *Phys. Rev.*, **75**, 1766.
IVANENKO, D., and RODICHEV, W., 1951, *Dokl. Akad. Nauk., U.S.S.R.*, **70**, 605.
MAYER, M. G., 1949, *Phys. Rev.*, **75**, 1969.
YANG, L. M., 1951, *Proc. Phys. Soc. A*, **64**, 632.

Angular Correlation in the Reaction ${}^6\text{Li}(d, p){}^7\text{Li}^*(\gamma){}^7\text{Li}$

The branching ratio in the slow neutron reaction ${}^{10}\text{B}(n, \alpha){}^7\text{Li}$ suggests a spin of 5/2 and odd parity for the 478 kev. excited state in ${}^7\text{Li}$ (Hanna and Inglis 1949); however, recent measurements have given isotropy within the experimental errors for the angular correlation between the alpha-particles and gamma-rays in this reaction (Rose and Wilson 1950) and for the angular distribution of the gamma-rays in the reaction ${}^7\text{Li}(p, p'){}^7\text{Li}^*(\gamma){}^7\text{Li}$ (Littauer 1950). This indicates a value 1/2 for the spin but is not quite conclusive (Inglis 1951), since chance values of the nuclear matrix elements, which cannot be calculated, might give very slight or zero correlation for higher spin. It is unlikely that this will happen with all the reactions leading to the excited state, and, therefore, it was thought worth while to measure the angular correlation between the protons and gamma-rays in the reaction ${}^6\text{Li}(d, p){}^7\text{Li}^*(\gamma){}^7\text{Li}$.

A thin target of ${}^6\text{Li}$ was bombarded with 630 kv. deuterons from the Cavendish 1 mev. high tension set, and the protons, detected by an anthracene screen and E.M.I. photomultiplier, type 5032, were observed at 90° to the incident beam. Another scintillation counter, using a solution of terphenyl in toluene, and capable of rotation in the plane perpendicular to the direction of the deuteron beam, was used to detect the gamma-rays. Proton-gamma coincidences were obtained with a resolving time of 15 millimicroseconds; the circuit was similar to that previously described (Curling and Newton 1950), but used secondary emission valves (E.M.I. type E.2133) as pulse limiters, the undelayed and delayed channels being fed from the anodes and secondary cathodes respectively. The average true-to-chance ratio during the experiment was 2:1 and the true counting rate three per second.

The number of proton-gamma coincidences per proton was determined at eight angles θ in the range 90° to 160° . No individual reading took more than two minutes, and the various angles were taken in as random an order as possible, so that any long-term drift in the apparatus should cancel out. In fact no such drift was observed. The results were corrected for absorption in the target holder, scattering and mechanical imperfections, by measuring the angular distribution of the gamma-rays from the reaction ${}^7\text{Li}(p, p'){}^7\text{Li}^*(\gamma){}^7\text{Li}$. This must be isotropic in the plane perpendicular to the proton beam.

From the known lifetime of the excited state (Elliot and Bell 1949), the average velocity of the recoiling nucleus at the instant of emission, and hence the centre-of-mass and Doppler corrections were calculated. After all corrections had been applied the result was fitted to a curve of the form $A + B \cos^2 \theta$ by the method of least squares, and the correlation coefficient B/A calculated to be $-2.7 \pm 2.5\%$. (If no centre-of-mass and Doppler

correction is applied the result is $-1.8 \pm 2.5\%$.) Thus within the limits of accuracy of this experiment there is no evidence for the angular correlation being anything other than isotropic, or the spin of ${}^7\text{Li}^*$ having any other value than $1/2$.

If the spin of ${}^7\text{Li}^*$ is other than $1/2$ some correlation is expected since the protons are known to have angular momenta up to 3 (Dunbar and Hirst 1951). In particular, if it is $5/2$ (odd) there should be a correlation of the form $1 + C \cos^2 \theta + D \cos^4 \theta$, most likely with $C \gg D$, because the magnetic dipole strength is expected to be about 200 times larger than that of the electric quadrupole (Inglis 1951).

Since three experiments of this type all suggest isotropic correlations to quite a good order of accuracy, the evidence for the spin of the 478 kev. excited state of ${}^7\text{Li}$ being $1/2$ now seems quite strong. This value is also in agreement with that predicted by the shell model (Mayer 1950).

I wish to thank Sir John Cockcroft and the Atomic Energy Research Establishment for providing the separated ${}^6\text{Li}$ target.

Cavendish Laboratory,
Cambridge.
1st August 1951.

J. O. NEWTON.

- CURLING, C. D., and NEWTON, J. O., 1950, *Nature, Lond.*, **166**, 339.
DUNBAR, D. N. F., and HIRST, F., 1951, *Phys. Rev.*, **83**, 164.
ELLIOT, L. G., and BELL, R. E., 1949, *Phys. Rev.*, **76**, 168.
HANNA, S. S., and INGLIS, D. R., 1949, *Phys. Rev.*, **75**, 1767.
INGLIS, D. R., 1951, *Phys. Rev.*, **81**, 914.
LITTAUER, R. M., 1950, *Proc. Phys. Soc. A*, **63**, 294.
MAYER, MARIA G., 1950, *Phys. Rev.*, **78**, 16.
ROSE, B., and WILSON, A. R. W., 1950, *Phys. Rev.*, **78**, 68.

A Study of Metal Transfer during Sliding, using Radioactivation Analysis

A number of methods have been used for detecting the fragments transferred when one metal slides on another, and a comprehensive review has been given by Burwell (1947). One of the most common methods involves the sliding of a radioactive metal over a non-radioactive surface, the transfer of activity to this surface being measured. I have recently had occasion to use a method based on a different principle, that of radioactivation analysis.

A copper surface was slid over a steel surface, and as a result some copper fragments were transferred to the steel. The steel specimen was then activated in a nuclear pile, the B.E.P.O. at Harwell, and within a few hours of its removal from the pile an autoradiograph was made of its surface, an exposure of ten seconds being given. The autoradiograph showed a light fogging corresponding to radiation from the iron in the steel, and a few intensely black spots produced by the copper fragments adhering to the steel surface (Figure 1). It will be seen that, if the method is to be successful, there must be a large difference in the specific activities of the two metals. Here the difference is by a factor of more than 4,000 (copper : 50 mc/gm., iron : 11 $\mu\text{c/gm.}$) (Isotope Division, Harwell, 1950).

In this particular case it also proved possible to detect the steel fragments transferred to the copper surface during sliding. The copper surface was also activated in the pile, and an autoradiograph was obtained some two weeks after its removal from the pile. By this time the activity due to the copper had practically disappeared (half-life of ${}^{64}\text{Cu}$ = 12.8 hours) whilst that of the steel had been reduced but little (half-life of ${}^{55}\text{Fe}$ = 3 years, of ${}^{59}\text{Fe}$ = 47 days). An exposure of three days showed up the steel fragments quite well, there being a background due to impurities in the copper (Figure 2). It is important in this experiment that the metal present in bulk does not contain appreciable amounts of impurities that are strongly activated in the pile, or else the background will be too high.

The autoradiographs, of clean surfaces of area $1\frac{1}{2}$ cm², slid under a load of 2 kg. at a speed of 0.1 cm/sec. for a distance of 0.5 cm., show that copper transfer to the steel has been in the form of some ten fragments ranging in size from 3×10^{-8} to 10^{-8} gm., as estimated from the amount of blackening by the method of Rabinowicz and Tabor (1951). The steel fragments in the copper have been far more numerous and widespread, there being perhaps 100 with mass in the range 3×10^{-8} to 3×10^{-9} gm. The two sets of fragments do not correspond spatially.

It is usually considered that the softer metal of a combination, in this case the copper, will wear away much more than the harder one, the steel. In these experiments the copper fragments have the greater mass whilst the steel fragments are more numerous, and it is not possible to draw definite conclusions, except perhaps that hardness is not the only factor that determines the wear.

The procedure used in this experiment has several advantages over the standard method of measuring metal transfer during sliding: (a) It facilitates the use of large sliding

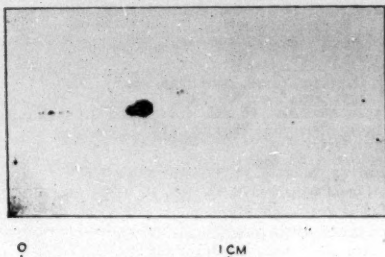


Figure 1. Autoradiograph of mild steel surface showing a number of copper fragments; some background fogging is visible in the corners.

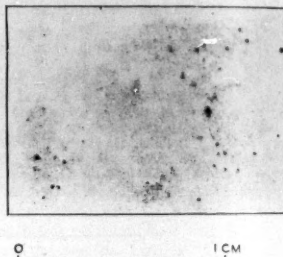


Figure 2. Autoradiograph of copper surface showing a large number of steel fragments as well as background fogging.

specimens, since strongly radioactive specimens need at no stage be handled in the friction laboratory. (b) It eliminates the problems which arise when, as so often happens, it is required to clean a specimen by removing metal to produce a fresh surface. If the specimen is radioactive, the procedure may be very hazardous. (c) Since very little handling of the surfaces after irradiation is required—they have merely to be placed on the photographic film and later removed—it is possible to carry out sliding experiments at leisure and later activate the various specimens at one time. This is of importance when the sliding experiments are time-consuming and the required isotope has a short half-life. (d) If, as in these experiments, fragments in both surfaces can be detected, it becomes possible to measure metal transfer in both directions during one experiment.

I wish to thank Dr. F. P. Bowden and Dr. D. Tabor for their encouragement of this work, and the Department of Scientific and Industrial Research for a maintenance grant.

Research Laboratory on the Physics and Chemistry of
Rubbing Solids,
Department of Physical Chemistry, Cambridge.*
1st August 1951.

E. RABINOWICZ.

BURWELL, J. T., 1947, *Nucleonics*, **1**, No. 4, 38.

ISOTOPE DIVISION, A.E.R.E., HARWELL, 1950, *Radioactive Materials and Stable Isotopes*, Catalogue No. 2.

RABINOWICZ, E., and TABOR, D., *Proc. Roy. Soc. A*, in the press.

* Now at the Lubrication Laboratory, Department of Mechanical Engineering, Massachusetts Institute of Technology.

The Theory of Oriented Overgrowth of Crystals

Smollett and Blackman (1951) have investigated the stability of a monolayer of an alkali halide, on the surface of another alkali halide, with its ions in the positions of the continuing lattice of the substrate, except for a uniform normal displacement. The result of the calculation is that these configurations are unstable in a number of cases which are known to form oriented overgrowths. This result is interpreted as showing that the theory of Frank and van der Merwe cannot account for these experimental results.

The theory put forward by Frank and van der Merwe (1949) was that a prerequisite for the formation of oriented crystal overgrowths is the initial formation of a monolayer coherent in periodicity with the underlying lattice. This does not require that the configuration of the monolayer should be identical with that of an interior layer of the substrate crystal: indeed, the contrary must be anticipated in general, even for a crystalline substance growing on itself, for the configuration of a surface layer of NaCl is certainly different from that of an interior layer of NaCl by reason of the Verwey displacements (see below).

Frank and van der Merwe employed a simple model of similar particles on a substrate with a different natural spacing to find the order of magnitude of the greatest misfit in which coherence of periodicity between monolayer and substrate would be retained in stable or metastable configurations. When the parameters of the model were adjusted to correspond to a Lennard-Jones inert gas model, critical misfits of 9% for stability and 14% for metastability were found; with larger misfits coherence is lost by formation of dislocations between monolayer and substrate, i.e. by a general expansion or contraction of the monolayer, coupled with inhomogeneous deformations.

Smollett and Blackman investigate another problem. They consider a model representing an infinite monolayer of one alkali halide deformed to the configuration of an interior layer of a second one, and placed on the surface of a semi-infinite crystal of the latter. Their elegant methods allow them to discover the limits of stability of their model against small homogeneous deformations only. Non-uniform displacements normal to the surface, and dislocations, are thus both excluded *a priori*. It is found that if the positive or negative misfit is conceptually increased from zero, instability first appears in shearing deformations. These instabilities can be given a simple physical interpretation. When the monolayer is unduly compressed, the repulsive forces between its ions become dominant, requiring a change of two-dimensional crystal structure to a closer packing. When the monolayer is unduly extended the repulsive forces are inadequate for its stability, and the ions of opposite sign must tend to approach each other to form ion pairs. If restricted to homogeneous deformations, the monolayer can only reveal these tendencies by commencing one or other of its principal shearing deformations. If it were reasonable to retain the supposition that positive and negative ions of the monolayer lie in the same plane, while allowing inhomogeneous two-dimensional deformations, we could infer that Smollett and Blackman have calculated an *upper* limit to the degree of misfit permitting stability in the proposed configuration.

Molière, Rathje and Stranski (1948, 1949) calculate that inhomogeneous displacements producing ion pairs occur even in the surface layers of some of the alkali halides by themselves. While the present writer believes that this particular result arises from defects of the model used, it is clear from their theory that the same ought to happen when an alkali halide monolayer is deposited on the surface of an alkali halide of larger lattice spacing. On the other hand, a plausible equilibrium configuration for the excessively compressed monolayer is one in which alternate rows of ions parallel to a cube edge are shifted in opposite directions along their length. However, before reaching any definite conclusion in either case one should pay attention also to inhomogeneous displacements normal to the crystal surface. According to Verwey (1946) these are important in the surface layer of any alkali halide; the positive and negative ions lie at different levels. The principal cause is ionic polarization, which becomes important in a surface layer. This is disregarded by Smollett and Blackman. It is considered by Molière *et al.*, who, however, disregard the difference between positive and negative ions, while neither considers inhomogeneous displacements normal to the surface.

Some day all these considerations may be taken into account in a way which has not yet been attempted: i.e. a combination of the approaches of Verwey and Molière *et al.*, possibly made more brief and elegant by borrowing from the mathematical methods of Smollett and Blackman. We shall then know, provided the crystal model employed is an adequate approximation, what is the equilibrium configuration of a surface monolayer of specified composition when constrained to have the periodicity of the underlying lattice. Then we shall be left with the question: does it stably retain this coherence? The only model yet available with which to attempt an answer to this question, crude as it may be, is that of Frank and van der Merwe. The writer supposes that it gives the correct order of magnitude for critical misfit, irrespective of the complications.

Smollett and Blackman's Table 2 requires no comment except with reference to the entries (2a)—cases in which parallel overgrowth occurs in spite of drastic differences in lattice parameter. Pending a searching experimental examination, the most natural supposition would be that these have a similar explanation to that given by Menzer (1938) for the case of silver on sodium chloride—the intervention of a layer of submicroscopic twins.

The writer must express his thanks to Drs. Smollett and Blackman for allowing him to see a copy of their manuscript in advance of publication.

H. H. Wills Physical Laboratory,
University of Bristol.
24th July 1951.

F. C. FRANK.

FRANK, F. C., and VAN DER MERWE, J., 1949, *Proc. Roy. Soc. A*, **198**, 216.

MENZER, G., 1938, *Naturwiss.*, **26**, 385.

MOLIÈRE, K., RATHJE, W., and STRANSKI, I. N., 1948, *Z. Phys.*, **124**, 421, 429; 1949, *Discussions of the Faraday Society*, No. 5, 21.

SMOLLETT, M., and BLACKMAN, M., 1951, *Proc. Phys. Soc. A*, **64**, 683.

VERWEY, E. J. H., 1946, *Rec. Trav. Chim. Pays-Bas.*, **65**, 521.

In his comments on our paper (Smollett and Blackman 1951) Dr. Frank has raised two points, one of a theoretical nature. In the cleavage plane of an alkali halide there will be a different position of the positive and negative ions in a direction perpendicular to the surface. It is suggested that this may affect our conclusions markedly.

This effect, attributed by Frank to Verwey (1946), has been discussed by Madelung (1916), who made experiments, without success, to show the existence of the double layer which is expected to form when rocksalt is cleaved.* The magnitude of the dipole moment, as calculated by Verwey for rocksalt, is, in the writer's opinion, too large to account for the experimental observation of Tull (1951), that the mean inner potential of rocksalt was the same when flat (100), (110) and (111) surfaces were used. Nor is it clear how this type of distortion of the surface could stabilize a highly unstable configuration.

This point is conceded, in part, by Frank in that he advances another explanation for the existence of apparently large misfits (20–50%: Table 2(b) of our paper); the contact plane of the deposit and substrate is supposed to be some plane other than the cube plane, and subsequent twinning leads to cube planes appearing parallel to the substrate surface. In support of this purely *ad hoc* assumption, Frank quotes the suggestion of Menzer (1938), in an analogous case where silver is deposited on to a cleavage face of rocksalt. This appears to be a (100) orientation with a misfit of 27%—again a 'drastic' case.

As this suggestion by Menzer has been used before (van der Merwe 1949) and seems to serve the Frank–van der Merwe theory as a saving clause, it is not irrelevant to point out that at least two independent investigations (Raether 1951, Tull 1951), using the electron diffraction technique, have shown that the contact plane of the silver is indeed the cube plane. The misfit of 27% must therefore be taken seriously.

Frank has emphasized, as we have also done, the need for further experiments. Some are already in progress in the Physics Department of this College. Attention should also be directed to those experimental results already available. Uyeda (1942) has evaporated a layer of silver, of mean thickness 5 Å., on to the cleavage (001) surface of molybdenite. The

electron diffraction pattern shows the (111) plane of the silver to be parallel to the surface of the substrate (there being two equivalent orientations), and the breadth of the silver 'spots' shows that the size of the silver crystals is only 15 Å. The 'side-spacing' of the silver is normal and differs appreciably from that of the substrate, the diffraction pattern from which is also visible. There is here no question of a 'pseudomorphic' layer. The misfit involved is 9%.

Another experimental investigation (Lucas 1951) on a thin coherent film of ZnO, grown chemically on a cleavage face of zinc, also shows the normal ZnO electron diffraction pattern as well as the pattern from the underlying zinc. The thickness of the layer is less than 25 Å. Here again there is no trace of the initial 'pseudomorphic' layer demanded by the Frank-van der Merwe theory.

I am indebted to Dr. D. W. Pashley for drawing my attention to the work of Uyeda, and to Dr. Frank for sending me his comments.

Physics Department,
Imperial College, London S.W. 7.
8th August 1951.

M. BLACKMAN.

- LUCAS, L. N. D., 1951, *Ph.D. Thesis*, London; see also *Proc. Phys. Soc. A*, **64**, 943.
MADELUNG, E., 1916, *Phys. Z.*, **20**, 494.
MENZER, G., 1938, *Z. Kristallogr.*, **99**, 378.
VAN DER MERWE, J. H., 1949, *Discussions of the Faraday Society*, No. 5, 201.
RAETHER, H., 1951, *Ergebn. exakt. Naturw.*, **24**, 121.
SMOLLETT, M., and BLACKMAN, M., 1951, *Proc. Phys. Soc. A*, **64**, 683.
TULL, V. F. G., 1951, *Proc. Roy. Soc. A*, **206**, 219.
UYEDA, R., 1942, *Proc. Phys.-Math. Soc. Japan*, **24**, 809.
VERWEY, E. J. H., 1946, *Rec. Trav. Chim. Pays-Bas.*, **65**, 521.

The Structure of Thin Layers of Zinc Oxide Grown on a Zinc Single Crystal

Finch and Quarrell (1933, 1934) reported some electron diffraction experiments which they interpreted as showing that the growth of very thin layers of zinc oxide on zinc resulted in the crystal lattice of the oxide being deformed by the influence of the base metal to give a structure differing from that of zinc oxide in bulk. They concluded that the basal (001) planes of the oxide grew parallel to the corresponding planes of the zinc so as to fit exactly, there being a corresponding expansion along the *c*-axis of the overgrowth so that the volume of the unit cell remained unchanged.

This conception of 'basal plane pseudomorphism', as it was termed by its authors, has recently been brought into prominence. It forms an essential part of the mechanism of oriented chemical growth as discussed by Cabrera and Mott (1949) in terms of the theory put forward by Frank and van der Merwe (Frank and van der Merwe 1949, van der Merwe 1949). However, the idea has been by no means universally accepted, and in particular the interpretation of the above-mentioned zinc oxide experiments (the principal experimental evidence for its validity) is open to doubt, as has already been pointed out (Thomson and Cochrane 1949). In view of these considerations it seemed highly desirable to carry out some further experiments in the hope of producing more conclusive evidence of the nature of very thin films of zinc oxide on zinc.

The best line of attack on the problem appeared to lie in the use of single crystals of zinc. These crystals have the useful property of cleaving parallel to (001) planes and so giving, in a relatively simple manner, the plane of most interest in the present investigation. Moreover, this one plane can then be studied without the experiment being confused by effects from other crystal planes.

The first cleavage faces of zinc that were studied by electron diffraction were found to be covered by an oriented layer of zinc oxide. This layer showed the normal structure but, as in the similar experiments reported by Raether (1950), no electron diffraction pattern

could be obtained from the underlying zinc crystal, and so it was only possible to estimate a lower limit for the thickness of the oxide. However, with improvement in the techniques of cleaving and mounting specimens it was found that the time of exposure of a fresh surface to air at atmospheric pressure could be reduced to less than one minute. When such a specimen was examined with a 55 kv. electron beam the pattern of Figure 1 was obtained.

Figure 2 shows how the pattern of Figure 1 may be split up into its components. The dots represent the zinc pattern, and the circles that of the zinc oxide. Since the zinc oxide completely covers the surface of the zinc (no zinc pattern being obtained at 30 kv.) the diffracted beams emerging from the metal must pass through a layer of the zinc oxide before reaching the photographic plate. In doing so they may be expected to be diffracted a second time in the oxide, giving an oxide pattern around each metal spot as primary. In general these secondary diffracted beams would be difficult to detect on account of their weakness, but in the production of Figure 1 the crystal was set so that much of the diffracted intensity was thrown into the beam giving the large spot on the centre line, with the result that the secondary pattern arising from this beam as primary may be seen. This secondary pattern is indicated by strokes in Figure 2.



Figure 1. Reflection pattern from zinc cleavage surface covered by a very thin layer of zinc oxide. $[110]$ azimuth.

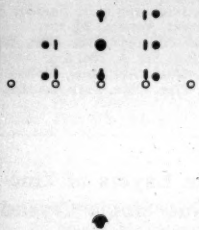


Figure 2. Analysis of pattern of Figure 1.

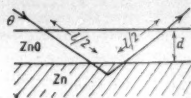


Figure 3.

The fact that an electron diffraction pattern can be obtained from the zinc mother crystal through the overlying layer of zinc oxide makes it possible to set an upper limit to the thickness of this layer. Thus if d (Figure 3) is the oxide thickness, l the total path length of the electron beam in the oxide, and θ the angle of incidence of the beam, $2d = \theta l$. In its passage through the lattices the beam is of course weakened, and with sufficient path length it will become so diminished that no detectable pattern will be obtained from the metal substrate. On the basis of transmission experiments Raether (1950) estimates that the maximum path length in zinc oxide for electrons with the energies used in electron diffraction work is 500 to 1,000 Å. That is to say, with l greater than this value no zinc pattern would be obtained through the overlying zinc oxide. Therefore, by taking the value of 1,000 Å. for l and putting $\theta = 0.05$, which was the minimum value for which a zinc pattern was obtained, we get $d_{\max} = 25$ Å., which can be put as an upper limit to the thickness of the oxide film grown in this experiment.

Thus the experiment shows that an extremely thin zinc oxide layer has been grown, no more than ten molecular layers thick. Such conditions are most favourable for the detection of the pseudomorphic layer suggested by Finch and Quarrell, and yet the oxide clearly shows its normal structure, with no trace of the pseudomorphic spacings. The experiment provides no support for the views of Cabrera and Mott (1949) and of Frank and van der Merwe (1949), which have also been objected to on theoretical grounds (Smollett and Blackman 1951). A fuller account of the work which is reported in part in this note is in preparation.

The writer gratefully acknowledges that the undertaking of this work was made possible by the granting to him of a Gleddon Travelling Fellowship by the University of Western Australia. He also wishes to thank Professor Sir George Thomson, under whose direction the work was carried out, and Drs. M. Blackman and D. W. Pashley for their interest and encouragement.

Physics Department,
Imperial College, London S.W.7.
9th August 1951.

L. N. D. LUCAS.

- CABRERA, N., and MOTT, N. F., 1949, *Rep. Progr. Phys.*, **12**, 163 (London: Physical Society).
FINCH, G. I., and QUARRELL, A. G., 1933, *Proc. Roy. Soc. A*, **141**, 398; 1934, *Proc. Phys. Soc.*, **46**, 148.
FRANK, F. C., and VAN DER MERWE, J., 1949, *Proc. Roy. Soc. A*, **198**, 205, 216.
VAN DER MERWE, J., 1949, *Discussions of the Faraday Society*, No. 5, 201.
RAETHER, H., 1950, *J. Phys. Radium*, **11**, 11.
SMOLLETT, M., and BLACKMAN, M., 1951, *Proc. Phys. Soc. A*, **64**, 683.
THOMSON, G. P., and COCHRANE, W., 1939, *Theory and Practice of Electron Diffraction* (London: Macmillan).

On the Mechanical Action in Dielectrics

In my account of this subject (Smith-White 1949) I have taken the mechanical force density $\mathbf{F}$ acting in a dielectric to be

$$\mathbf{F} = (\mathbf{P} \cdot \nabla) \mathbf{E}, \quad \dots\dots (1)$$

where $\mathbf{P}$ is the polarization of the dielectric and $\mathbf{E}$ is the electric force in the dielectric. Cade (1951) has objected that the formula (1) does not take account of the fact that a volume element, at the position of $\mathbf{E}$, itself provides a contribution to the field of the same order as $\mathbf{E}$, so that in finding the force on the element this contribution must be subtracted. This view of the matter, which is a common one, is due to misunderstanding. The point is a subtle one, and it has not been elucidated before. I regard (1) and the associated formula

$$\mathbf{G} = \mathbf{P} \times \mathbf{E} \quad \dots\dots (2)$$

for the couple density as *the fundamental formulae* in the development of a mathematical theory of dielectric behaviour, based on a proper interpretation of the Poisson-Kelvin hypothesis. Cade does not object to (2).

According to the hypothesis mentioned, the behaviour of dielectrics under electrical influence may be accounted for by assuming that each volume element dv of the dielectric acquires an electric moment $\mathbf{P} dv$; this I take to mean that a dielectric body, considered from the macroscopic point of view, behaves, in electrostatics, as though it were simply a continuous volume distribution of electric moment with density $\mathbf{P}$. On this view we are faced with the theoretical problem of determining the behaviour of continuous distributions of polarity; and until this question is decided the Poisson-Kelvin hypothesis as stated above does not furnish any theory of dielectrics at all.

In electrostatic theory we ordinarily contemplate the following kinds of electrical distributions: (i) discrete distributions of point electric charges, $q_1, \dots, q_n$; (ii) continuous distributions of electricity defined by a charge density ρ ; (iii) discrete distributions of point electric dipoles, $\mathbf{p}_1, \dots, \mathbf{p}_n$; (iv) continuous distributions of electric polarity defined by a moment density $\mathbf{P}$. Now the primitive electrostatic law prescribes the mechanical action on each element in the type (i). But it does not apply directly to give the mechanical action on the elements in any of the other kinds of distribution. It is easy to infer the appropriate extensions of Coulomb's law which enable us to specify this action on the elements of distributions (ii) and (iii). This, however, involves an extension of the primitive hypothesis of the same kind as that emphasized by Kellogg (1929) in connection with the application of Newton's law of gravitation to continuous distributions of matter. On the other hand, if we try to write down the mechanical force which acts on an element of the distribution (iv), by an integration over the distribution of a contribution from each of the other elements, we find that the integral which presents itself does not converge.

If a theory of electrical distributions of type (iv) is to be in line with the theories of the other three types of distribution it must be developed from a hypothesis concerning the mechanical action on the elements of the distribution. As just mentioned, the obvious procedure for finding such a hypothesis fails. There is, however, another course open to us, and this can be regarded as a uniform procedure for all four types of distribution. We begin by noting that the mechanical action on the elements in (i), (ii) and (iii) may be specified in an alternative, mathematically equivalent, way by first introducing the potential function ϕ , then defining the electric field $\mathbf{E} = -\nabla\phi$, and then specifying, for (i) that the force acting on a charge q is $q\mathbf{E}$, for (ii) that the force density acting at a place where the charge density is ρ is $\rho\mathbf{E}$, for (iii) that the force acting on a dipole $\mathbf{p}$ is $(\mathbf{p} \cdot \nabla)\mathbf{E}$, and the couple acting on a dipole $\mathbf{p}$ is $\mathbf{p} \times \mathbf{E}$.

In line with these specifications for distributions (i), (ii), and (iii) we can specify the mechanical action on an element of the distribution (iv). Suppose the distribution occupy the volume v . Define the potential by

$$\phi = \int_v \mathbf{P} \cdot \nabla \left(\frac{1}{r} \right) dv, \quad \dots\dots (3)$$

the electric field by $\mathbf{E} = -\nabla\phi$. We now assert that the force density acting on an element of the distribution is given by (1) and the couple density acting on it is given by (2). These statements amount to a hypothesis which I regard as the appropriate extension of Coulomb's law for point charges, enabling us to construct a mathematical theory of distributions of electric polarity. The value of this hypothesis for the physics of dielectrics is to be judged by a comparison of its consequences with the actual behaviour of bodies. As I have shown, one consequence of this theory is that it enables us to express the conservation of energy in dielectrics in a more satisfactory way than has been done before.

Thus the formulae (1) and (2) constitute my interpretation of the analytical significance of the Poisson-Kelvin hypothesis. Formula (3) is a mere mathematical auxiliary to the statements (1) and (2). In the literature of electrical theory (1) and (2) are generally neglected, while formula (3) is usually supposed to embody the whole content of the Poisson-Kelvin hypothesis. Transforming (3) by Green's theorem, if f be the boundary of v , we get

$$\phi = \int_f \frac{P_n}{r} df - \int_v \frac{\text{div } \mathbf{P}}{r} dv, \quad \dots\dots (4)$$

where P_n is the component of $\mathbf{P}$ directed along the outward normal to f . This formula is usually interpreted by saying that the moment distribution is equivalent to a surface charge distribution of density $\sigma = P_n$, and a volume charge distribution of density $\rho = -\text{div } \mathbf{P}$. These are Poisson's equivalent distributions. On this interpretation we would be justified in translating the fundamental hypothesis to the form "dielectrics under electrical influence behave as though they were distributions of electrical charge". Few physicists would accept the statement in this form, and the notion of equivalent charge distributions is in fact a fundamental mistake. Poisson's distributions are equivalent only as regards the potential function ϕ ; they are not equivalent as regards the mechanical effects.

Finally, I remark that if we develop in detail the theory of point dipole distributions and compare it with the theory of continuous distributions of polarity based on formulae (1) and (2) we see that the two theories are mathematically similar. We may note that in the case of systems of hypothetical point dipoles there is no analogue to the Poisson's equivalent charge distributions, and it is not possible to make the error which has confused electrical theory for so long. Moreover, the subtle difficulties in the formulation of a theory of continuous moment distributions are of no real consequence for physics. If we refer to such distributions as a matter of mathematical convenience we must only be sure that our theory of them is properly parallel to the theory of discrete distributions.

Department of Mathematics,
University of Sydney.
24th July 1951.

W. B. SMITH-WHITE.

CADE, R., 1951, *Proc. Phys. Soc. A*, **64**, 665.

KELLOGG, O. D., 1929, *Foundations of Potential Theory* (Berlin: Springer), pp. 22, 80.

SMITH-WHITE, W. B., 1949, *Phil. Mag.*, **40**, 466; see also 1950, *Nature, Lond.*, **166**, 689; 1951, *Ibid.*, **167**, 401; 1951 a, *Proc. Roy. Soc. N.S.W.*, **85**, Part 1.

The Long-Range Tritons from the Reaction ${}^9\text{Be}(d, t){}^8\text{Be}$

The emission of tritons as a result of the bombardment of beryllium with 1 mev. deuterons was identified chemically by O'Neal and Goldhaber (1940). Using an ionization chamber, Williams, Haxby and Shepherd (1937) measured, at 225 kev. deuteron energy, the range of the tritons emitted from a thick (5 cm. air equivalent) beryllium foil. The energy of the reaction was thus estimated to be 4.32 ± 0.06 mev., which is about 7% less than that calculated from the masses given by Tollestrup, Fowler and Lauritsen (1950). Recently Resnick and Hanna (1951) have reported a value of 4.61 ± 0.04 mev. for this reaction energy which is in agreement with the value given from the masses.

In the present experiment, the photographic plate method was used in detecting the particles emitted from a beryllium foil of thickness 0.4 cm. air equivalent due to bombardment by a deuteron beam of 7.70 mev. mean energy. For this purpose a camera described by Rotblat, Burrows and Powell (1951) and Ilford C2 photographic plates with emulsion 200μ thick were employed.

Search was made for the long-range tritons from the reaction where the residual nucleus ${}^8\text{Be}$ was left in the ground state. Apart from the general appearance of a triton track by comparison with a proton track in the emulsion, the group of tritons was identified

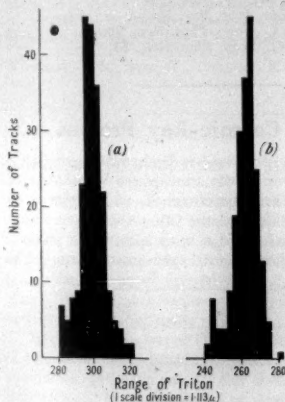


Figure 1. Range distribution of tritons from the ground state transition of the reaction ${}^9\text{Be}(d, t){}^8\text{Be}$ with 7.70 mev. deuterons (a) at 20° (b) at 40° .

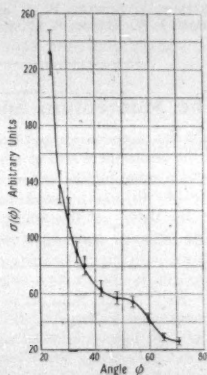


Figure 2. Angular distribution in the centre-of-mass system ground state transition of the reaction ${}^9\text{Be}(d, t){}^8\text{Be}$ with 7.70 mev. incident deuterons.

by the agreement of the Q -values calculated for different angles of emission. Measurements were carried out for eleven different angles in the region from 20° to 60° with respect to the direction of the incident deuterons and representative histograms at angle 20° and 40° are shown in Figure 1. For each angle of observation, the group was fitted with a gaussian curve from which the mean range and half width were measured. Since the tracks were dipping in the emulsion, the true range was derived from the known mean angle of approach of these particles to the examined area of the photographic plate. Also, a correction to the energy of the emitted triton due to its passage through the thin beryllium foil was made for each angle of measurement. Using the range-energy curve (El-Bedewi 1951) the mean energy of the triton group was found. The Q -values were thus calculated for different angles of observation and the mean value for the present reaction can be stated as 4.67 ± 0.03 mev., thus confirming the work of Resnick and Hanna (1951).

Also, the angular distribution of this triton group was studied by counting the number of tracks belonging to each of the plotted histograms. By knowing the area examined in the photographic plate, together with its mean distance from the target, the relative intensity of the tritons emitted at each angle of observation could be calculated. The results

were then transferred to the centre-of-mass system and represented as shown in Figure 2. This distribution is based on measurements of a total of 2,000 tracks over eleven angles at intervals of $2\frac{1}{2}^\circ$ or 5° .

The marked rise of the cross section near the forward direction is interesting, since it suggests that the mechanism of this reaction is a single stage process having a similarity to the mechanism of deuteron stripping (Butler 1950), in which a proton or a neutron is removed from the impinging deuteron without the formation of a compound nucleus, or rather to the inverse of this process. In other words, the deuteron was presumably to be regarded as sucking out a neutron during its passage past the target nucleus. If the deuteron were first absorbed to form a compound nucleus, a more or less symmetrical angular distribution would be expected.

Nuclear Physics Research Laboratory,
The University of Liverpool.
12th July 1951.

F. A. EL-BEDEWI.

BUTLER, S. T., 1950, *Phys. Rev.*, **80**, 1095.

EL-BEDEWI, F. A., 1951, *Proc. Phys. Soc. A*, in the press.

O'NEAL, R. D., and GOLDBABER, M., 1940, *Phys. Rev.*, **57**, 1086.

RESNICK, I., and HANNA, S. S., 1951, *Phys. Rev.*, **82**, 463.

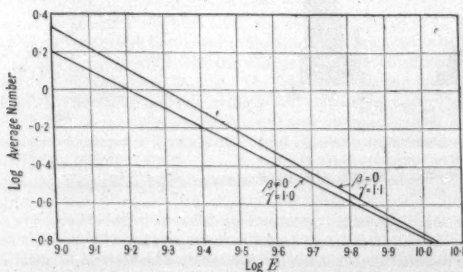
ROTLAT, J., BURROWS, H. B., and POWELL, C. F., 1951, *Proc. Roy. Soc. A*, in the press.

TOLLESTRUP, A., FOWLER, W. A., and LAURITSEN, C. C., 1950, *Phys. Rev.*, **78**, 372.

WILLIAMS, J. W., HAXBY, R. O., and SHEPHERD, W. G., 1937, *Phys. Rev.*, **52**, 1031.

The Momentum Spectrum of Cosmic-Ray Protons

Recently the momentum spectrum of cosmic-ray protons has been measured both at the top of the atmosphere and at sea level. At the top of the atmosphere Winckler *et al.* (1950) found a value for the exponent of the differential spectrum of -1.9 ± 0.05 in the range 10^3 to 14×10^3 mev. Van Allen and Singer (1950) give the value -2.1 for a similar range. In his theory of the nucleon cascade Messel (1951 a, b, c) has used a value of 2.1 and has obtained good agreement with a wide range of experimental data. This



The graph gives the computed momentum spectrum of protons at sea level for an incident power law integral spectrum of exponent -1.1 . The upper curve is obtained neglecting ionization loss β . The lower curve includes ionization loss.

theory, however, predicts that an incident power law should be reproduced throughout the atmosphere for all energies above the cut-off if ionization loss is neglected. If ionization loss is taken into account the spectrum is slightly flattened. We have computed the sea level spectrum for the energy range 10^3 to 10×10^3 mev., using an incident power law spectrum of exponent -2.1 for both cases. The results are given in the Figure. It will be seen that in this range the points are well fitted by a power law of exponent 2.0 when ionization loss is included.

The sea level spectrum has recently been measured by Mylroï and Wilson (1951). From their data using a least squares method we have computed the power law whose exponent

gives the best fit. For the region 0.6×10^3 to 6×10^3 Mev. we obtain the result 2.5 ± 0.2 and for the region 10^3 to 6×10^3 Mev., 2.8 ± 0.3 . The errors which give the 50% width have been calculated on the assumption that there is no error in the momentum determination and that the fluctuation in the numbers is gaussian. Both these assumptions are not strictly true and the actual errors therefore will be somewhat larger. However, these results are sufficiently in disagreement with the prediction of the theory to make it likely that the initial assumption of a power law at the top of the atmosphere is incorrect. To produce agreement we would have to assume that for energies higher than 15×10^3 Mev. the spectrum falls off more quickly than a power law of exponent -2.1 . This would also be in agreement with the conclusions of Hilberry (1941), although his method of arriving at this result is open to criticism.

We wish to thank Dr. T. E. Nevin and Mr. Franklin for their assistance, and Dr. J. G. Wilson for helpful discussion.

School of Cosmic Physics,
Dublin Institute for Advanced Studies.
1st August 1951.

C. B. A. McCUSKER.
H. MESSEL.

HILBERRY, N., 1941, *Phys. Rev.*, **60**, 7.

MESSEL, H., 1951 a, *Proc. Phys. Soc. A*, **64**, 726; 1951 b, *Phys. Rev.*, **83**, 21; 1951 c, *Comm. of the Dublin Institute for Advanced Studies, Series A*, No. 7.

MYLROI and WILSON, 1951, *Proc. Roy. Soc. A*, **64**, 404.

VAN ALLEN, J. A., and SINGER, S. F., 1950, *Phys. Rev.*, **78**, 819.

WINCKLER, J. R., STIX, T., DWIGHT, K., and SABIN, R., 1950, *Phys. Rev.*, **79**, 656.

Residual Resistance in an Extremely Impure Semiconductor

In a previous paper (Wright 1951), it has been shown that cadmium oxide can act as an 'impurity metal' type of semiconductor, i.e. the concentration of free electrons n_f which is due mainly to excess Cd atoms in interstitial positions in the lattice, is independent of the temperature. It is considered that the impurity centres are so dense that they are always ionized in an impurity metal. The electrons are free in an impurity conduction band. Pearson and Bardeen (1949) have suggested that such a state of affairs also exists in very impure specimens of silicon.

In the previous paper (Wright 1951) it was shown that theoretical treatment of the case of a constant concentration of free electrons in an ionic lattice indicated that the resistivity should be proportional to the absolute temperature, if the specimen were sufficiently degenerate. This was found to agree extremely well with the experimental results given for CdO.

Investigation has continued, and interesting results have been observed with specimens containing an extremely large excess of Cd. The specimens were produced by pressing pure anhydrous CdO powder in moulds and sintering in air. The temperature of sintering appears to be very crucial. At temperatures of 550 – 650°C . there occurs in the specimen a colour change from brown to black which is reversible, but if the temperature is increased to 700 – 800°C . the change becomes irreversible and, upon cooling, the specimen is found to be dull black-purple in colour. This colour is probably due to the large excess of Cd in the lattice, and it is with these specimens that we are concerned here. The conductivity is extremely high, and the variation of the resistivity with temperature of such a specimen is shown in the Figure.

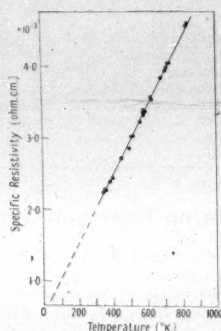
It will be seen that the results fit accurately an equation of the form

$$\rho = A + BT = 5.39 \times 10^{-4} + 4.76 \times 10^{-6} T.$$

The term proportional to the temperature in the equation is likely to be the same as that obtained in the theory given previously. As the temperature falls below the Debye temperature Θ , this part of the resistance due to the normal scattering by the lattice is no longer proportional to the temperature, and should tend towards a constant value of $B\Theta/2$ as the temperature approaches 0°K . However, the origin of the constant A is of interest. It bears a direct analogy to the residual resistance in impure metals. A possible

explanation of A is the presence of intergranular boundaries, since the specimen originated from powder. It is likely that such a mechanism would be strongly dependent upon the temperature. Therefore, it seems probable that A is due to scattering by the impurity centres which are defects in the lattice, but which are also the sources of the electrons. The mean free path due to scattering by such ionized impurities has been investigated by Conwell and Weisskopf (1950), and was found to be dependent upon the square of the energy of the electron above the bottom of the conduction band. In CdO, since it is an impurity metal, all the impurities are ionized, leaving no non-ionized impurities which must be neglected on Conwell and Weisskopf's theory. The considerations are simplified still further, since the electron gas is extremely degenerate, so that only the electrons possessing energies near the Fermi energy E^* are effective in conduction, and E^* varies but slowly with temperature. The effective energy, and thus the mean free path l_i for scattering by impurities, are therefore independent of temperature to a first approximation.

Thus $1/l_i = n_i Q_i$ where Q_i is the effective area of cross section of scattering, and n_i is the concentration of both free electrons and impurity centres. Q_i is dependent upon



Graph of resistivity against absolute temperature for black-purple CdO specimen containing much excess Cd.

the dielectric constant, the effective mass of the electrons, E^* and n_i , but is independent of temperature. Since the degeneracy is high, this leads us to the simple expression for $A = h e^{-2} (3n_i/8\pi)^{1/3} Q_i$. Assuming a probable value for $n_i \sim 5 \times 10^{20}$ we deduce that $Q_i \sim 4.4 \times 10^{-15}$, or that the effective radius of the impurity centre is $(Q_i/\pi)^{1/2} \sim 3.8 \times 10^{-8}$ cm. The average distance apart of such centres is of the order of 12×10^{-8} cm.

The transition from semiconductor to 'impurity metal', as observed by Pearson and Bardeen (1949) in silicon has yet to be satisfactorily explained. A certain amount of importance may therefore be attached to Q_i , since it is a measure of the 'sphere of influence' of the impurity centre when in an impurity metal. It is hoped that from further investigation of the conductivity of samples of CdO with different amounts of impurity content, and also of the Hall effect or thermoelectric power which will give the concentration of free electrons n_i , accurate values of Q_i may be obtained, which may enable light to be thrown upon the problem of transition.

Physics Department,
University College,
Ibadan, Nigeria.
25th April 1951.

R. W. WRIGHT.

- CONWELL, E., and WEISSKOPF, V. F., 1950, *Phys. Rev.*, **77**, 388.
PEARSON, G. L., and BARDEEN, J., 1949, *Phys. Rev.*, **75**, 865.
WRIGHT, R. W., 1951, *Proc. Phys. Soc. A*, **64**, 350.

REVIEWS OF BOOKS

Einführung in das Studium der Physik, by W. FINKELNBURG. Pp. 128. (Heidelberg: Carl Winter, 1950.) DM 4.50; bound in cloth DM 6.30.

This interesting booklet is meant to be a guide for prospective German physicists. It contains a little of everything: the aims and problems in physics, the history of physical thought, the methods of research, the University syllabus, the main sections in physics and the type of person likely to be an ideal physicist. There is a chapter on the physicist in various professions which is, alas, the weakest chapter of all. It contains contributions by several sub-authors about the physicist as academic and school teacher, industrial researcher, employee in the electrical and chemical industries and about women physicists. A chapter is included on physical literature listing textbooks, handbooks and periodicals, and giving an introduction into the international decimal classification. Finally there are some notes about the German learned societies and professional bodies.

In Germany physicists are trained at universities and technical academies. During the first two years (=4 semesters) 14 to 18 hours per week are spent on lectures on compulsory subjects and about three hours on optional subjects apart from the time for practical work and seminars. At the end of that period a preliminary diploma examination is taken. During the following two years the number of lectures is reduced and the time for practical and seminar work increased. At the end of this period the diploma examination (or teaching examination) is taken; this requires a miniature thesis but not original research. A further two years spent on original research are necessary to complete a dissertation and after an examination in the form of our *viva*, the degree of Dr.Phil. or Dr.Ing. is awarded.

One cannot help feeling that in those chapters in which the author 'advises' his future colleagues, the dogmatic element becomes sometimes so strongly pronounced that it makes rather amusing reading; for example he says, "anyone who wants to stick to fixed working hours and wants to be left alone in the evenings or spend his spare time on a hobby, should abandon the idea of ever becoming a good physicist". The author's only support for this opinion is that of a well-known mathematician who once said that "modern physics is actually much too difficult for physicists".

May I suggest that the author mentions in a future edition the value of personal contact by attending meetings at home and abroad, of a knowledge of foreign languages, and last but not least, the need of a revival of the travelling scholar.

A. VON ENGL.

Selected Topics in X-Ray Crystallography, edited by J. BOUMAN. (Monographs on Theoretical and Applied Physics, III.) Pp. xv+375. (Amsterdam: North Holland Publishing Company, 1951.) 38s.

The preface of this volume accurately describes it as a series of partly interrelated monographs, bearing on several applications of x-ray diffraction. The monographs have been prepared by members of the Delft X-Ray Institute, and have been edited by Professor J. Bouman.

The work is divided into eight sections, of which the first, Section A, deals with general methods, and includes chapters by Professor Bouman on the reciprocal lattice and the use of reciprocal space in discussing problems in x-ray optics, and a chapter by Dr. van Reijen on errors due to the termination of Fourier series. Section B deals with distortion in crystals, including under that heading not only the effects of the cold-working of metals, but also of thermal agitation. Section C deals with twinning, and the rate of nucleation during the recrystallization of aluminium, Section D with the x-ray investigation of photographic emulsions, and Section E, by Professor J. A. Prins, with the amorphous states of certain elements. Section F deals with quantitative work with powders, with special reference to problems of absorption and focusing, Section G with the crystallization of natural rubber, and Section H with certain biological investigations.

The method of presentation as a series of separate monographs, while sometimes allowing technical details to be discussed more fully than would be possible in a general textbook of comparable length, makes the logical development of the arguments more difficult, and leads inevitably to a certain amount of overlapping, although this is not always

disadvantage. The introductory theoretical section is interesting, and on the whole lucidly set out; but it is not clear why the sharp distinction is made between reciprocal space and Fourier space in Chapter I. By reciprocal space, the author of the chapter appears to mean the reciprocal lattice, whereas by Fourier space he means the reciprocal lattice with its points weighted by the appropriate values of the structure factors, that is to say the values of the Fourier transform of the unit cell, at those points of reciprocal space which correspond to the reciprocal lattice points. The distinction is perhaps a little arbitrary, for the reciprocal lattice is the Fourier transform in reciprocal space of the point lattice upon which the crystal is built up, and the weighted reciprocal lattice the Fourier transform of a periodic continuous distribution of matter based upon that lattice when the number of unit cells approaches infinity.

The book gives a very interesting account of the various lines of research carried out by this most active school of x-ray crystallography. It is very well produced, and the printing and diagrams are excellent.

R. W. J.

Crystal Growth, by H. E. BUCKLEY. Pp. xv + 571. (New York: Wiley and Sons; London: Chapman and Hall, 1951.) 72s.

This book deserves a place in the library wherever crystals are grown or studied. It has useful chapters on the various methods of artificial preparation of crystals and on habit modification by impurities—the author's most particular interest—the latter supported by an appendix of detailed information on this subject. A miscellany of significant and sometimes little known observations about crystals are scattered through the work, or collected in the later chapters. The extensive bibliographies, despite important omissions, are a particularly valuable feature.

A considerable amount of space is devoted to historical accounts of the earlier theories of crystal growth and relevant crystal properties, moderately complete up to about 1930. These accounts nearly always lack precision, and are frequently quite wrong: the reader will do well to use them as guides to the literature only.

The author's information on discoveries made since 1930 is quite astonishingly scrappy, whether it has to do with progress in the theory of the solid state, who invented the electron microscope, or (what one might have expected to be within his sphere) the plain facts about the supercooling of water. In the circumstances, the reviewer must be gratified that his own contribution to the theory of crystal growth receives mention at all.

F. C. FRANK.

Theory of Electrons, by L. ROSENFELD. Pp. xv + 119. (Amsterdam: North Holland Publishing Company, 1951.) 15s.

For half a century successive generations of honours physics students have experienced the delight of reading for the first time H. A. Lorentz's classical work *The Theory of Electrons*. Professor Rosenfeld's book of a similar title worthily sustains the high standard set by its celebrated predecessor.

After a short historical introduction the second chapter discusses how the electric and magnetic polarization densities of Maxwell's equations for material media are related to the structural properties of atoms as expressed by their electric and magnetic dipole moments. The modification of atomic charge and current distributions under the influence either of external fields or of the mutual interaction between atomic systems is then discussed, and the ground thus cleared for a very stimulating treatment of magnetism, electrical polarization, and dispersion, in subsequent chapters.

The treatment is classical throughout but care has been taken to point out where this approach is inadequate and the modifications required by quantum theory are mentioned. It aims not so much to give a detailed account of the electric, magnetic and optical properties of matter, but rather to examine and clarify the underlying principles on which the interpretation of these properties is based. In this aim the author has been eminently successful. The approach is physical rather than mathematical but when mathematical formalism is introduced it is distinguished by the elegance and clarity we have learned to associate with Professor Rosenfeld's writings.

The book is based on a course of lectures given at Manchester and one feels envious of the students privileged to attend such a course. It will certainly constitute essential reading for advanced students and research workers in physics for many years to come.

E. H. S. BURHOP.

Heat and Thermodynamics, by J. K. ROBERTS, revised by A. R. MILLER. Pp. xx+593. 4th Edition. (London: Blackie and Son, 1951.) 35s.

The book by Roberts has become a classic in its field, used by several generations of students since it first appeared in 1928. It contained adequate information on practically any branch of its subject for all but specialists, and gave very clear and useful treatment of theory.

This fourth edition has been revised by Dr. Miller of Cambridge. Without sacrificing the characteristic features of the original work, he has brought it up to date, especially in the field of low-temperature physics, where, after all, the main advances have taken place.

It gives a very clear account of the science of heat, and can be highly recommended to all students prepared to work hard enough to master it.

J. H. A.

The Elements of Thermodynamics, by CHARLES FABRY, translated by G. F. Herrenden Harker. Pp. x+229. (London: Frederick Muller, 1951.) 15s.

This is a very lucid introduction to the basis of thermodynamics, classically considered and presented, with some account of its application to physics and chemistry, as distinct from engineering. It does not include any account of the statistical mechanical approach, nor of Carathéodory's presentation of the classical theory, but within these limits is very useful. The translation appears to be very good and certainly does not betray itself as translation, but, if it is faithful, then the original is much less limpid than we hope for and often find in French writing.

Others may not agree with me, but for myself I see no reason why time need be spent on the translation of scientific work from French to English at all, especially when the result has to be sold at such a relatively high price. Every science student ought to be able to read this in French without real difficulty.

J. H. A.

Theory and Application of Infinite Series, by KONRAD KNOPP. 2nd English Edition. Pp. xii+563. (London: Blackie and Son, 1951.) 35s.

This second edition is a translation of the second German edition revised in accordance with the fourth German edition. As the only essential difference between the second and fourth German editions is a new chapter on Euler's summation formula and asymptotic expansions already included in the first English issue, the two English editions differ only in some improvements and simplification of proofs. The references to literature have been brought up to date.

Professor Knopp's work is a well-established standard textbook on infinite series with two special features. One is the simplicity of the proofs in spite of the highest mathematical rigour maintained throughout. The second feature is an attempt to develop the subject in a systematic way for which we should be grateful to the author since our knowledge about infinite series mainly consists of separate bits of information. In particular, the various tests of convergence and divergence are presented in a masterly way. The price paid for rigour and coherence is an elaborate presentation of the idea of real number and of sequences of such numbers in the first two chapters (over 100 pages), including a detailed account of the notion of limit. The discussion is kept on a high logical level with good commonplace description of the notions involved. Irrationals are defined through Dedekind cuts. Mathematicians will find this first part rather indispensable and physicists may turn to those pages to learn the why and wherefore of many proofs.

The second part, Chapters III-VIII, gives an excellent account of the elementary properties of infinite series dealing with the ratio and root tests, power series, especially those of elementary functions, infinite products, and the transformation of series for numerical evaluation. The text is full of well-chosen illustrative examples followed by carefully grouped and graded exercises.

The third part, Chapters IX-XIV, is the development of the theory, first for positive terms, complete and beautifully presented, then for arbitrary and variable terms including uniform convergence and Fourier series, and for complex terms leading to the definition of elementary functions for complex variable and to Dirichlet, faculty and Lambert series.

In Chapter XIII, on divergent series, the special processes of summation known by the names Cesaro, Hölder, Abel and Euler are extensively dealt with but the systematization of such processes by infinite matrices is not included. The last chapter deals with Euler's summation formula and with asymptotic expansions.

Bibliography and general index complete this excellent treatise in Miss R. C. H. Young's pleasant translation. A word of warning: 'Application' in the title does not mean physical or geometrical application. It really means the application of general results to important particular cases like Stirling's formula or Dirichlet series. The production of the book is first rate.

PAUL DIENES.

CONTENTS FOR SECTION B

	PAGE
Prof. SYDNEY CHAPMAN. Some Phenomena of the Upper Atmosphere. (Presidential Address)	833
Prof. L. G. H. HUXLEY. A General Formula for the Conductivity of a Gas containing Free Electrons	844
Dr. L. ESSEN and Dr. K. D. FROOME. The Refractive Indices and Dielectric Constants of Air and its Principal Constituents at 24,000 Mc/s.	862
Mr. D. H. PEIRSON. Alpha-Particle Assay and the Measurement of the Thorium-Uranium Ratio in Radioactive Ores	876
Dr. C. N. DAVIES and Miss MARY AYLWARD. The Trajectories of Heavy, Solid Particles in a Two-Dimensional Jet of Ideal Fluid Impinging Normally upon a Plate	889
Miss P. ROTHWELL. Fluctuations in the Energy-Loss of Fast Electrons in a Proportional Counter	911
Mr. W. L. HARRIES and Dr. A. VON ENGEL. The Mechanism of the Low-Frequency Electrodeless Discharge in Chlorine and the Influence of Irradiation	916
Letters to the Editor:	
Mr. R. PARKER. The Saturation Magneto-Resistance of Iron-Aluminium Alloys	930
Mr. W. P. OSMOND. The Magnetic Properties of α -Ferric Oxide	931
Reviews of Books	932
Contents for Section A	934
Abstracts for Section A	935

ABSTRACTS FOR SECTION B

Some Phenomena of the Upper Atmosphere, by SYDNEY CHAPMAN. (Presidential Address.)

ABSTRACT. The height distribution of the atmosphere depends on the temperature and the mean molecular weight of the air; recent progress in our knowledge of these two quantities will be reviewed, the main sources of information being outlined. The motions (winds and tides) in the upper atmosphere will similarly be considered.

The main gross uncertainty regarding composition at high levels relates to the proportion of atomic nitrogen present. Besides the major constituents that chiefly determine the mean molecular weight, there are important rare constituents, such as ozone, sodium and hydroxyl, which reveal their presence by their absorption or emission spectra; and there are others whose presence can be inferred from theirs.

The composition of the atmosphere changes by escape from the top (hydrogen and helium) and, by addition, from below (e.g. helium and carbon dioxide) and, as shown by the auroral spectrum, from above (hydrogen); cosmic rays also both add to the atmosphere and produce changes of composition by nuclear reactions.

Near the magnetic equator there are important ionospheric phenomena not yet fully explored and explained. Among these one of the most interesting is the abnormal intensification of electric current flow, specially notable over Huancayo in Peru.

A General Formula for the Conductivity of a Gas containing Free Electrons, by
L. G. H. HUXLEY.

ABSTRACT. This paper contains a general discussion of electron drift in gases according to the method of free paths in which a fallacy contained in some earlier treatments is avoided. A general formula is derived for drift velocity in an electric field which is an arbitrary function of the time, and from it formulae for drift velocities in the following special cases of importance are deduced: drift in a constant electric field, in an alternating sinusoidal field, in a constant electric field with an applied magnetic field, in an alternating electric field with an applied magnetic field. Formulae for the electrical conductivity of an electron-laden gas follow from those for the drift velocities. Applications of the formulae to ionospheric and other studies are mentioned.

The Refractive Indices and Dielectric Constants of Air and its Principal Constituents at 24,000 Mc/s., by L. ESSEN and K. D. FROOME.

ABSTRACT. The refractive indices of air and its principal constituents have been measured at a frequency of 24,000 Mc/s. with a precision comparable with that obtained in the optical range. The method is based on the measurement of the resonant frequency of a cavity resonator first when it is filled with the gas and then when it is evacuated. The source of oscillations used is a Pound-stabilized velocity-modulated oscillator, and its frequency is measured by reference to a high harmonic of a quartz standard, with a precision of 1 part in 10^8 . The cavity is provided with a tuning plunger, which changes the resonant frequency through a range of about 10 Mc/s., and is calibrated to an accuracy of within 1 kc/s.

Most of the measurements were made by the frequency-change method and the plunger was used in a narrow region only for a precise setting to resonance. It is possible by a larger movement of the plunger to compensate for the whole frequency change due to the removal of the gas and thus to work at a fixed frequency.

The following results were obtained for $(n-1)10^6$ where n is the refractive index at 0° C., 760 mm. Hg: dry CO₂-free air, 288.15 ± 0.1 ; nitrogen, 294.1 ± 0.1 ; oxygen, 266.4 ± 0.2 ; argon, 277.8 ± 0.2 ; carbon dioxide, 494 ± 1 ; and the value for water vapour at 20° C., 10 mm. Hg pressure was 60.7 ± 0.1 .

The dielectric constants can be calculated from the relationship $\mu\epsilon = n^2$, where μ is the magnetic permeability and ϵ the dielectric constant, the values of $(\mu-1)10^6$ being taken as 0.4 for air, 1.9 for oxygen and zero for the other gases.

Accurate formulae are given for obtaining the refractive index of moist air at different atmospheric conditions, and are reduced to the following simple formula which is applicable for normal atmospheric conditions:

$$(n_{t,p}-1)10^6 = \frac{103.49}{T} p_1 + \frac{177.4}{T} p_2 + \frac{86.26}{T} \left(1 + \frac{5748}{T}\right) p_3,$$

where p_1, p_2, p_3 are the partial pressures of dry air, carbon dioxide and water vapour, t is the temperature in degrees C., and $T=273+t$ is the absolute temperature. A value of $1.839 \pm 0.002 \times 10^{-18}$ E.S.U. was derived for the dipole moment of the water vapour molecule.

Alpha-Particle Assay and the Measurement of the Thorium-Uranium Ratio in Radioactive Ores, by D. H. PEARSON.

ABSTRACT. The measurement of the alpha-particle activity of a 'thick' radioactive source containing the natural radioactive series is discussed critically.

Two methods of determining the thorium-uranium ratio are considered for use in ore or mineral assays. The energy discrimination method is simple in procedure and can take account of lack of secular equilibrium between members of a series in the radioactive sample. The beta-alpha coincidence method, making use of the difference in the disintegration constants of radium C' and thorium C', is more complicated.

Initial experimental verification of the theory has been obtained. The estimated statistical error in determining the thorium-uranium ratio by the energy discrimination method is $\pm 5\%$ in the region of $Th/U=1$, with a 4% sample (U₂O₃ equivalent concentration) in 4 minutes counting. A similar accuracy is obtainable in the coincidence method with a counting period 10 times greater.

The Trajectories of Heavy, Solid Particles in a Two-Dimensional Jet of Ideal Fluid Impinging Normally upon a Plate, by C. N. DAVIES and MARY AYLWARD.

ABSTRACT. An expression is derived for the flow field in a two-dimensional jet of ideal fluid impinging normally upon a plate situated at an arbitrary distance from a parallel-sided orifice. Numerical data are given when the orifice is at an infinite distance and in three other cases. In each example the trajectories of solid particles carried by the fluid are calculated by a stepwise method, and the conditions determining whether a particle will strike the plate or not are found.

Fluctuations in the Energy-Loss of Fast Electrons in a Proportional Counter, by P. H. M. ROTHWELL.

ABSTRACT. The fluctuations in the energy lost by fast electrons over a fixed small fraction of their range have been studied by measuring the pulses the electrons produce in passing through a proportional counter. The energy loss distribution calculated theoretically by Landau is approximately gaussian with a high-energy tail. The experimental distribution is in agreement with the theoretical on the high-energy side of the peak, but is wider than Landau predicts on the low-energy side; this discrepancy is greater in krypton than in argon. The experimental values of the most probable energy loss agree with the theoretical values.

The Mechanism of the Low-Frequency Electrodeless Discharge in Chlorine and the Influence of Irradiation, by W. L. HARRIES and A. VON ENGEL.

ABSTRACT. The current flowing through a 50 c/s. electrodeless discharge in a short cylindrical glass vessel with plane electrodes at the ends filled with chlorine at 5–50 mm. Hg was investigated with an oscillograph. It consists essentially of between one and fifty or more distinct pulses per half cycle, the number increasing with the voltage. At sufficiently large voltage these pulses cover the greater part of a half cycle including the instant of zero voltage. By irradiating the discharge with light from an incandescent lamp the average pulse height decreases, radiation below 4,800 Å. being strongly active. By irradiating only the central portion of the vessel the pulse height does not change. Irradiating one wall reduces the height of the pulses in every second half cycle, namely those pulses whose electron avalanches start from that wall.

Once the discharge starts, electric charges collect on the inner surface of the vessel. Each current pulse consists of a series of avalanches which develop between small areas of the inner glass walls. One such area may discharge within a half cycle in several steps. The time variation of the applied field, the wall-charge field and the field in the gas are discussed and a new mechanism is developed which appears to apply to discharges between solid dielectrics.

At room temperatures, chlorine molecules form an adsorbed layer, several molecules thick, on the glass walls. Irradiation produces photo-dissociation of Cl_2 , the atoms being effective in capturing electrons in this layer where slow electrons and many-body collisions are likely. This reduction of the number of secondary electrons reduces the pulse height. Adsorbed molecular gas layers also explain observations at higher temperatures. At higher voltages the interval between two successive pulses becomes so small that one pulse reduces the height of the following one. This is probably due to metastable Cl atoms and resonance radiation diffusing to the wall where they cause dissociation of molecules in the adsorbed layers, the chlorine atoms capturing electrons as before. It also explains why at high voltages the effect of irradiation becomes insignificant.